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ELEMENTS

OF

CHEMISTRY,

INCLUDING THE

APPLICATIONS OF THE SCIENCE IN THE ARTS.

BY

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ELEMENTS

OF

CHEMISTRY.

ORDER IV.

METALS PROPER HAVING PROTOXIDES ISOMORPHOUS WITH MAGNESIA.

SECTION I.

MANGANESE.

Eq. 27·67 *or* 345·9; Mn.

THIS element is found in the ashes of plants, in the bones of animals, and in many minerals, of which that employed in the preparation of oxygen is one of the richest. The black oxide of manganese was long known as *magnesia nigra*, from a fancied relation to magnesia alba; but was first thoroughly studied by Scheele, in 1774, and immediately afterwards by Gahn, who obtained from it the metal now called manganese.

From its strong affinity for oxygen, and the very high temperature which it requires for fusion, manganese is one of the most difficult of all the metals proper, to reduce and fuse into a button. Hydrogen and charcoal, at a red heat, reduce the superior oxides of this metal to the state of protoxide, without eliminating the pure metal at that temperature; but at a white heat, charcoal deprives the metal of the whole of its oxygen. The following process is recommended by M. John for the reduction of manganese: it illustrates the chief points to be attended to in the reduction of the less tractable metals. Instead of a native oxide, an artificial oxide of manganese, obtained by calcining the carbonate in a well-closed vessel, is operated upon. This oxide, which is preferred from being in a high state of division, is mixed with oil and ignited in a covered crucible, so as to convert the oil into charcoal. After several repetitions of this treatment, the carbonaceous mass is reduced to powder, and made into a firm paste by kneading it with a little oil. Finally, this paste is introduced into a crucible lined with charcoal (creuset brasqué), the unoccupied portion of which is filled up with charcoal powder. The crucible is first heated merely to redness for half an hour, to dry the mass and decompose the oil; after which its cover is carefully luted down, and it is exposed for an hour and a half to the most violent heat of a wind-furnace that the crucible itself can support without undergoing fusion. The metal is obtained in the form of a semi-globular mass or button in the lower part of the crucible, but not quite pure, as it contains traces of carbon and silicon derived from the ashes of the charcoal. By igniting the metal a second time in a charcoal crucible, with a portion of borax, John obtained it more fusible and brilliant, and so free from charcoal that it left no black powder when dissolved in an acid.

Manganese is a greyish white metal, having the appearance of hard cast iron. Its density, according to John, is 8·013; while M. Berthier finds it to be 7·05, and Bergmann made it 6·850: according to Hjelm, it is 7·0. From its close resemblance to iron, manganese may be expected to be susceptible of magnetism; but its magnetic powers are doubtful. Péclet has endeavoured to show that manganese can assume and preserve magnetic polarity from the temperature — 4° up to 70°, but loses it again at higher temperatures. The small difference between the atomic weights of iron, manganese, cobalt, and nickel, which are respectively 28, 27·67, 29·52, and 29·57, is remarkable, attended as it is by a great analogy between these metals in many other respects.

Manganese oxidates readily in air, soon falling down as a black powder; in water it occasions a disengagement of hydrogen gas. It is best preserved in naphtha, like potassium, or over mercury. Manganese exhibits five degrees of oxidation, with two intermediate or compound oxides.

OXIDES OF MANGANESE.

Protoxide or manganous oxide	MnO.
Sesquioxide or manganic oxide	Mn_2O_3.
Bioxide or Peroxide	MnO_2.
Manganoso-manganic oxide or red oxide	Mn_3O_4, or $MnO + Mn_2O_3$.
Varvicite	Mn_4O_7, or $Mn_2O_3 + 2MnO_2$.
Manganic acid	MnO_3.
Permanganic acid	Mn_2O_7.

Protoxide of manganese; Manganous oxide; MnO, 35·67 *or* 445·9.—This is the oxide existing in the ordinary salts of manganese, which are isomorphous with the salts of magnesia. It may be obtained by fusing at a red heat in a platinum crucible, a mixture of equal parts of pure chloride of manganese and carbonate of soda, with a small quantity of sal-ammoniac. By the reaction between the first-mentioned salts, chloride of sodium is produced, together with the carbonate of manganese, which is decomposed at a red heat, leaving the protoxide of that metal. The hydrogen of the sal-ammoniac at the same time reduces to the state of protoxide any bioxide which may be formed by absorption of oxygen from the air. Any one of the superior oxides of manganese, in the state of fine powder, may be converted into protoxide by passing hydrogen gas over it, in a porcelain tube at a red heat: the bioxide obtained by igniting the nitrate of the protoxide of manganese was recommended by Dr. Turner as the most easily deoxidated.

Protoxide of manganese is a powder of a greyish green colour, more or less deep. When obtained by means of hydrogen at a low temperature, it absorbs oxygen from the air, soon becoming brown throughout its whole mass, and is, indeed, sometimes a pyrophorus; but when prepared by hydrogen at a high temperature, it acquires more cohesion, and is permanent.

Protoxide of manganese dissolves readily in acids, and is a strong base. Its salts are of a pale rose tint, which is not destroyed by sulphurous or hydrosulphuric acid, and must be considered as a peculiar character of manganous salts. When the solution is colourless, as it sometimes is, the fact is explained, according to M. Görgeu, by the presence of a salt of iron, nickel, or copper; the green or blue tint of the latter metals producing white or a scarcely perceptible violet shade when combined with the rose tint of a salt of manganese. *Caustic alkalies* added to solutions of manganous salts throw down the protoxide of manganese in the form of a white hydrate, which soon absorbs oxygen from the air and becomes brown; when collected on a filter and washed, it ultimately changes into a blackish brown powder, which is the hydrate of the sesquioxide. A similar change is instantaneously produced by the action of chlorine-water upon the white hydrate, or by the addition of chloride of lime to a salt of the protoxide of manganese: but then the hydrated bioxide is formed. Protoxide of manganese resembles magnesia and protoxide of iron, in being but partially precipitated by ammonia. The *alkaline monocarbonates* precipitate white carbonate of manganese, which does not turn brown in the air, and dissolves sparingly in a cold solution of sal-ammoniac. *Bicarbonate of potash* precipitates a strong solution immediately, and renders a dilute solution slightly turbid; but if the solution contains a free acid, so that an excess of carbonic acid is set free, no precipitate is formed. The earthy carbonates do not precipitate manganous salts. *Hydrosulphuric acid* forms no precipitate in neutral solutions of manganous salts containing any of the stronger acids. In a neutral solution of the acetate, a flesh-coloured precipitate is formed after some time; but not if the solution contains free acetic acid. *Sulphide of ammonium* forms in neutral solutions of manganous salts a flesh-coloured precipitate of hydrated sulphide of manganese, insoluble in excess of sulphide of ammonium, but readily soluble in acids. When exposed to the air, it turns brown on the surface, from oxidation. The least trace of iron or cobalt colours it black. *Ferrocyanide of potassium* forms in neutral solutions of manganous salts a white precipitate, having a tinge of red, and soluble in free acids. *Ferricyanide of potassium* forms a reddish precipitate, which is insoluble in acids. Manganous salts, and indeed all compounds of manganese, heated with *borax* or *phosphorus-salt* in the outer blowpipe flame, form an amethyst-coloured bead containing manganoso-manganic oxide, which becomes colourless in the inner flame by reduction of that oxide to the protoxide. This character distinguishes manganese from all other metals. The minutest trace of manganese is discovered by heating the solution with a little *bioxide of lead* and *nitric acid*, when a red tint appears due to the formation of permanganic acid (W. Crum). An equally delicate reaction is obtained in the dry way by heating the substance supposed to contain manganese with *carbonate of soda* on platinum foil in the outer blowpipe flame. The smallest trace of manganese is indicated by the formation of green manganate of soda. The delicacy of the reaction may be increased by adding a little nitre to the carbonate of soda.

Protosulphide of manganese may be procured in the dry way, by heating a mixture of bioxide of manganese and sulphur. Sulphurous acid is disengaged, and a green powder remains, which dissolves in acids with disengagement of hydrosulphuric acid. The same compound is obtained in the humid way, when acetate of manganese is decomposed by hydrosulphuric acid, or any manganous salt precipitated by an alkaline sulphide. Protosulphate of manganese, decomposed by hydrogen at a red heat, yields an oxisulphide. A crystalline sulphide is obtained by passing the vapour of bisulphide of carbon over hydrated manganic oxide ignited in a porcelain tube: the crystals are iron-black rhombic prisms, having a tinge of green, and yielding a dingy green powder (Völker).

Phosphide of manganese is obtained by exposing an intimate mixture of 10 parts of pure ignited bioxide of manganese, 10 parts of white-burnt bones, 5 parts of white quartz-sand, and 3 parts of ignited lamp-black for an hour in a closed Hessian crucible to a heat sufficient to melt cast-iron,—or by strongly igniting 10 parts of ignited phosphate of manganese, 3 parts of ignited lamp-black, and 2 parts of calcined borax in a crucible lined with charcoal. The product is a very brittle, crystalline regulus of the colour of grey cast-iron, and of specific gravity 5·951. It is permanent in the air, glows when heated in contact with air, and burns with an intense light when heated with nitre. It appears to contain Mn_5P, and is probably a mixture of Mn_3P and Mn_7P, the latter of which compounds is left behind when the substance is treated with hydrochloric acid, while the former dissolves, with evolution of non-spontaneously inflammable phosphuretted hydrogen (Wöhler).

Protochloride of manganese: $MnCl+4HO$; 63·17 + 36 *or* 789·63 + 450.—This salt crystallises in thick tables, which are oblong and quadrilateral, and of a rose colour; it is very soluble in water, and slightly deliquescent. The residuary liquid obtained in preparing chlorine by dissolving bioxide of manganese in hydrochloric acid, consists of chloride of manganese contaminated with a portion of sesquichloride of iron.

To remove the latter and obtain a pure chloride of manganese, the solution should be boiled down considerably to expel the excess of acid, diluted afterwards with water, and boiled again with carbonate of manganese, which salt precipitates the whole of the sesquioxide of iron, forming chloride of manganese with its acid (Everitt). If about one fourth of the impure solution of chloride of manganese be reserved, and precipitated by carbonate of soda, a quantity of carbonate of manganese will be obtained sufficient to precipitate the iron from the other three-fourths of the liquid, and applicable to that purpose after it has been washed. The iron may likewise be separated by evaporating the solution of the impure chloride to dryness, heating the residue to low redness in a crucible, as long as hydrochloric acid continues to escape; then leaving it to cool, exhausting with boiling water, and filtering. The hydrated chloride of iron is resolved by the heat into hydrochloric acid and sesquioxide, while the chloride of manganese remains unaltered, and is easily dissolved out by water, all the iron remaining behind. Chloride of manganese, when free from iron, is precipitated white, without any shade of blue, by ferrocyanide of potassium. The crystals retain one of their four equivalents of water at 212° (Brandes), but may be rendered anhydrous at a higher temperature. Brandes finds 100 parts of water to dissolve at 50°, 38·3; at 88°, 46·2; at 144·5°, 55 parts of the anhydrous salt. A higher temperature, instead of increasing the solubility of this salt, diminishes it. From the aqueous solution, chlorine, with the aid of heat, throws down the black hydrated bioxide of manganese. Hypochlorous acid produces a similar result, with evolution of free chlorine. Absolute alcohol dissolves half its weight of the anhydrous chloride of manganese, and affords, by evaporation in vacuo, a crystalline alcoate, containing two equivalents of alcohol.

Chloride of manganese forms two crystalline double salts with chloride of ammonium. One of these, $MnCl.NH_4Cl$, forms cubical crystals, containing 1 equiv. water, according to Rammelsberg, and 2 eq. according to Hauer. These crystals when ignited leave manganoso-manganic oxide in microscopic pyramids resembling Hausmanite. The other salt, $2MnCl.NH^4Cl+4HO$, forms crystals belonging to the oblique prismatic system (Hautz). Solution of chloride of manganese containing chloride of ammonium, yields, on addition of ammonia and exposure to the air, a precipitate of hydrated manganoso-manganic oxide (Otto).

Protocyanide of manganese is obtained in the form of a yellowish or reddish-white precipitate, on adding cyanide of potassium to the solution of a manganous salt. It quickly turns brown on exposure to the air. It is decomposed by the stronger acids, and dissolves in alkaline cyanides.

The corresponding *fluoride of manganese* forms, with fluoride of silicon, a double salt which is very soluble in water and crystallises in long regular prisms of six sides. The formula of this double salt is, according to Berzelius, $2SiF_3+3MnF+21HO$.

Carbonate of manganese is a white insoluble powder, which acquires a brown tint when exposed in the dry state at 140°. It is decomposed by a red heat. Carbonate of manganese occurs in the mineral kingdom, in the form of *manganese-spar*, but never in a state of purity, being mixed with the carbonates of lime and iron, which have the same crystalline form, viz. the rhombohedral. Its presence in spathic carbonate of iron is said to be the cause why the latter yields an iron peculiarly adapted for the manufacture of steel.

Protosulphate of manganese; Manganous sulphate; MnO,SO_3+7HO.—A solution of this salt, used in dyeing and entirely free from iron, is prepared by igniting bioxide of manganese mixed with about one-tenth of its weight of pounded coal in a gas retort. The protoxide thus formed is dissolved in sulphuric acid, with the addition of a little hydrochloric acid towards the end of the process; the sulphate is evaporated to dryness, and again heated to redness in the gas retort. The iron is found after ignition in the state of sesquioxide and insoluble, the persulphate of iron being decomposed, while the sulphate of manganese is not injured by the temperature of ignition, and remains soluble. The salt may also be obtained by heating bioxide of manganese, previously freed from the carbonates of lime and magnesia by boiling with dilute sulphuric acid, with an equal weight of strong oil of vitriol, and gently igniting the resulting mass for an hour, to decompose the sulphates of iron and copper formed at the same time. The manganous sulphate, which remains unaltered, is then dissolved in water, and the solution evaporated to the crystallising point. The solution is of an amethystine colour, and does not crystallise readily. When cloth is passed through sulphate of manganese and afterwards through a caustic alkali, protoxide of manganese is precipitated upon it, and rapidly becomes brown in the air; or it is peroxidised at once by passing the cloth through a solution of chloride of lime. The colour thus produced is called manganese-brown.

Crystallised under 42°, the sulphate of manganese gives crystals containing 7HO, which have the same form as sulphate of iron. The crystals which form between 45° and 68°, contain 5HO, and are isomorphous with sulphate of copper. By a higher temperature, from 68° to 86°, a third set of crystals is obtained, which contain 4HO : their form is a right rhombic prism. The sulphate of iron and other sulphates also assume the same form (Mitscherlich). This salt loses 3HO at 243°, but retains 1 eq. even at 400°, like the other magnesian sulphates. M. Kuhn finds, that when a strong solution of the sulphate of manganese is mixed with sulphuric acid and evaporated by heat, a granular salt is precipitated, which contains only one equivalent of water. This sulphate also forms with sulphate of potash a double salt containing 6HO. The anhydrous salt is soluble, according to Brandes, in 2 parts of water at 59°, in 1 part at 122°; but above the latter temperature, the salt becomes less soluble. The tetra-hydrated salt dissolves in 0·883 part of water at 43·3°; in 0·79 part at 50°; in 0·82 part at 65·8°; in 0·67 part at 99·5°; and in 1·079 part at 2·1°. Manganous sulphate is insoluble in absolute alcohol, but dissolves in 500 parts of spirit of the strength of 55 per cent.

Hyposulphate of manganese; $MnO . S_2O_5 + 6HO$. For the preparation, see I. 335.—The bioxide of manganese used in preparing it should be previously treated with nitric acid, to dissolve out the hydrated oxide, and be well washed. The salt forms rose-coloured, generally indistinct, crystals, belonging to the doubly oblique prismatic system (Marignac). The *oxalate of manganese* is a highly insoluble salt. The *acetate* is soluble in 3½ parts of cold water, and also in alcohol. Bitartrate of potash dissolves protoxide of manganese, and forms a very soluble double salt, the *tartrate of potash and manganese,* which can be obtained, although with difficulty, in regular crystals.

Sesquioxide of manganese; Manganic oxide; Mn_2O_3; 79·34 *or* 991·8.—This oxide is left of a dark brown, almost black colour, when the nitrate of the protoxide is gently ignited. It also occurs crystallised in the mineral kingdom, although rarely; its density is 4·818, and it is named *braunite* as a mineral species. The hydrate of manganic oxide is formed by the oxidation in air of manganous hydrate. Manganic hydrate also frequently occurs in nature of a black colour, both crystallised and amorphous, and is often mixed with the bioxide of manganese. It constitutes the mineral species *manganite,* of which the density is 4·3 to 4·4, and the formula Mn_2O_3, HO. This hydrate may be artificially prepared by heating finely divided bioxide of manganese with monohydrated sulphuric acid, decomposing the resulting manganic sulphate with water, and washing it thoroughly (Carius). This oxide colours glass of a red or violet tint. The common violet or purple stained glass contains manganic oxide; also the amethyst.

Manganic oxide is a base isomorphous with alumina and sesquioxide of iron. It dissolves in cold hydrochloric acid without decomposition. Concentrated sulphuric acid combines with it at a temperature a little above 212°, but does not form a solution. Dilute sulphuric acid does not dissolve it, either in the cold or when gently heated, unless manganous oxide is present, even in very small quantities, in which case a violet solution is formed; hence the commonly received statement that manganic oxide forms a red solution with sulphuric acid (Carius). At somewhat elevated temperatures, acids reduce the sesquioxide of manganese to protoxide, with evolution of oxygen.

Manganic sulphate; $Mn_2O_3 . 3 SO_3$.—Prepared by mixing finely divided bioxide of manganese (obtained by passing chlorine gas through a solution of carbonate of soda in which carbonate of manganese is suspended) with monohydrated sulphuric acid to the consistence of a pulp, and gradually heating the mixture in an oil-bath to about 276°, at which point the mass becomes dark green and more mobile. It is then drained on a plate of pumice-stone to remove the greater part of the sulphuric acid; afterwards stirred up in a warm basin with the strongest nitric acid (free from nitrous acid); again drained on pumice-stone; and this treatment repeated several times: lastly, it is dried in the oil-bath at 266°, and preserved in carefully dried tubes.—Manganic sulphate thus obtained is a dark green powder which exhibits no traces of crystallisation. It may be heated to 320° without decomposition, but at higher temperatures gives off oxygen and is reduced to manganous sulphate. At ordinary temperatures it is all but insoluble in concentrated sulphuric and nitric acid; with the former it may be heated nearly to the boiling point without alteration, but, when boiled with the acid, it dissolves as manganous sulphate, with evolution of oxygen.

Heated with concentrated nitric acid to 212°, it turns brown, but resumes its green colour when the acid is evaporated at the lowest possible temperature. In strong hydrochloric acid, it dissolves, like the pure sesquioxide, forming a brown solution, which when heated gives off chlorine till all the sesquioxide of manganese is reduced to protoxide. Organic substances, heated with the dry salt, decompose it with considerable violence. The salt absorbs moisture very rapidly, so that it must always be kept in sealed tubes. Small quantities of it deliquesce in a few seconds, forming a violet solution, which, however, soon becomes brown and turbid from separation of the hydrated oxide. Water decomposes the salt rapidly, especially when heated, separating the pure hydrated sesquioxide. Hence the mode of preparing the hydrate above mentioned. Sulphuric acid, somewhat diluted, decomposes manganic sulphate, converting it into a red-brown powder, which appears to be a basic salt.* Manganic sulphate forms an alum with sulphate of potash (Mitscherlich): this salt occurs native in needle-shaped crystals at Alum Point, on the Great Salt Lake in North America (L. D. Gale).

Sesquichloride of manganese (Mn_2Cl_3) is formed when the sesquioxide is dissolved in hydrochloric acid at a low temperature. The solution is yellowish brown or black, according to its degree of concentration, and is decomposed by a slight elevation of temperature, with evolution of chlorine. A corresponding *sesquifluoride* may be crystallised.

Sesquicyanide of manganese.—A compound of this cyanide is formed, when manganous acetate is mixed with hydrocyanic acid in excess, then neutralised with potash and evaporated. The manganous cyanide then absorbs oxygen, and is converted into hydrated manganic oxide and manganic cyanide, which last combines with cyanide of potassium, and appears, on the cooling of a concentrated solution, in red crystals, which dissolve easily in water (Mitscherlich). This salt is analogous to red prussiate of potash, containing manganese instead of iron, and may, therefore, be represented as containing manganicyanogen—a *manganicyanide of potassium*, $K_3(Mn_2Cy_6)$. As a double cyanide, its formula would be, $3KCy.Mn_2Cy_3$.

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* Carius, *Ann. Ch. Pharm.* xcviii., 53.

Red oxide of manganese, $MnO.Mn_2,O_3$, named by Berzelius manganoso-manganic oxide, is always produced when any oxide of manganese is heated strongly in air. It is a double oxide, being a compound of single equivalents of protoxide and bioxide of manganese. It forms the mineral *Hausmanite*, which differs from manganite in having manganous oxide in place of water. Its density is 4·722. Berthier finds that strong nitric acid dissolves out the protoxide of manganese from the red oxide, and leaves a remarkable hydrate of the bioxide, of which the formula is $4MnO_2 + HO$.

Bioxide or Peroxide of manganese; Black oxide of manganese; MnO_2; 43·67 *or* 545·9.—This is the well-known ore of manganese employed in the preparation of oxygen and chlorine. It generally occurs massive, of an earthy appearance, and contaminated with various substances, such as sesquioxide of iron, silica, and carbonate of lime; but sometimes of a fibrous texture, consisting of small prisms radiating from a common centre. Its density varies from 4·819 to 4·94; as a mineral species it has been named *pyrolusite*.* Another important variety of this ore, known as *wad*, is essentially a hydrate, containing, according to Dr. Turner, 1 eq. of water to 2 eq. of peroxide. A hydrated bioxide, consisting of single equivalents of its constituents, is formed by precipitating the protosalts of manganese with chloride of lime; and the same compound results from the decomposition of the acids of manganese, when diluted with water or an acid. It is possible that the equivalent of this oxide should be doubled, and that its proper formula is Mn_2O_4, corresponding with peroxide of chlorine, ClO_4.

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* From πυρ, fire, and λυω, I wash; in allusion to its being employed to discharge the brown and green tints of glass.

Bioxide of manganese loses one-fourth of its oxygen at a low red heat, and is changed into sesquioxide; at a bright red heat it loses more oxygen, and becomes red oxide, the condition into which all the oxides of manganese pass when ignited strongly in the open air. The bioxide does not unite either with acids or with alkalies. When boiled with sulphuric acid, it yields oxygen gas and a sulphate of the protoxide. In hydrochloric acid it dissolves with gentle digestion, evolving chlorine gas, and forming protochloride of manganese (page 6). It is extensively used in the arts for preparing chlorine, and also to preserve glass colourless by its oxidating action. In the last application, it is added to the vitreous materials in a relatively small proportion, and becomes protoxide, which is not a colouring oxide, while as sesquioxide it would stain glass purple. At the same time it destroys carbonaceous matter, and converts protoxide of iron, which colours glass green, into sesquioxide, which is less injurious.

The mineral *varvicite* was discovered by Mr. R. Phillips among some ores of manganese from Hartshill in Warwickshire. It is distinguished from the bioxide by being much harder, having more of a lamellated structure, and by yielding water freely when heated to redness. Its density is 4·531. It may be supposed to consist of 1 eq. of sesquioxide, and 2 eq. of bioxide with 1 eq. of water (Dr. Turner); its formula is, therefore, $Mn_2O_3 . Mn_2O_4 + HO$.

VALUATION OF BIOXIDE OF MANGANESE.

The numerous applications of the higher oxides of manganese depending upon the oxygen which they can furnish, render it important to have the means of easily and expeditiously estimating their value for such purposes. The value of these oxides is exactly proportional to the quantity of chlorine which they produce when dissolved in hydrochloric acid, and the chlorine can be estimated by the quantity of protosulphate of iron which it oxidises. Of pure bioxide of manganese 43·7 parts (1 eq.) produce 35·5 parts of chlorine, which oxidise 278 parts (2 eq.) of crystallised protosulphate of iron. Hence 50 grains of bioxide of manganese yield chlorine sufficient to oxidise 317 grains (more exactly, 316·5 grs.) of protosulphate of iron.

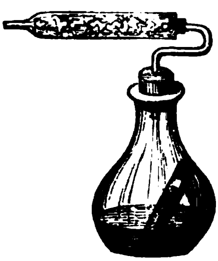
50 grains of the powdered oxide of manganese to be examined are weighed out, and also any known quantity, not less than 317 grains, of the sulphate of iron (copperas) employed in chlorimetry. The oxide of manganese is thrown into a flask containing an ounce and a half of strong hydrochloric acid, diluted with half an ounce of water, and a gentle heat applied. The sulphate of iron is gradually added in small quantities to the acid, so as to absorb the chlorine as it is evolved; and the addition of that salt continued, till the liquid, after being heated, gives a blue precipitate with the red prussiate of potash, and has no smell of chlorine, which are indications that the protosulphate of iron is present in excess. By weighing what remains of the sulphate of iron, the quantity added is ascertained; say *m* grains. If the whole manganese were bioxide, it would require 317 grains of sulphate of iron, and that quantity would, therefore, indicate 100 per cent. of bioxide in the specimen; but if a portion of the manganese only is bioxide, it will consume a proportionally smaller quantity of the sulphate, which quantity will give the proportion of the bioxide, by the proportion: as 317 : 100 :: *m* : per-centage required. The per-centage of bioxide of manganese is thus obtained by multiplying the number of grains of sulphate of iron oxidised by 0·317. It also follows that the per-centage of chlorine which the same specimen of manganese would afford, is obtained by multiplying the number of grains of sulphate of iron oxidised by 0·2588.

Another mode of estimation is to pass the chlorine gas, obtained by heating the manganese in a flask with hydrochloric acid, into a solution of sulphurous acid, quite free from sulphuric (it should give no precipitate with chloride of barium); the chlorine converts an equivalent quantity of sulphurous acid into sulphuric. The liquid is then mixed with chloride of barium, and boiled to expel the excess of sulphurous acid, after which the sulphate of baryta is thrown on a filter, washed, dried, ignited, and weighed. The 116·64 gr., or 1 eq. of sulphate of baryta, correspond to 43·7 gr., or 1 eq. of bioxide of manganese.

The value of commercial oxide of manganese may also be estimated by heating it with hydrochloric acid and oxalic acid. The disengaged chlorine then converts the oxalic acid into carbonic acid,—2 eq. of carbonic acid representing 1 eq. of chlorine, and therefore 1 eq. of bioxide of manganese:

$$C_2HO_4 + Cl = 2CO_2 + HCl.$$

Fig. 1.



A convenient apparatus for the determination is a small light glass flask (fig. 1), of 3 or 4 oz. capacity, having a lipped edge, and fitted with a perforated cork. A piece of tube, about 3 inches long, drawn out at one end, and filled with fragments of chloride of calcium, to absorb water, is fitted by means of a small cork and a bent tube to the mouth of the flask. A short tube closed at one end, and small enough to go into the flask, is used to contain the hydrochloric acid. Fifty grains of the mineral, in the state of very fine powder, are introduced into the flask, together with about half an ounce of cold water, and 100 grains of strong hydrochloric acid in the tube, as shown in the figure: 50 grains of crystallised oxalic acid are then added, the chloride of calcium tube fitted on, and the whole quickly weighed. The flask is then tilted so as to allow the hydrochloric acid to flow out of the tube, and come in contact with the mixture of manganese and oxalic acid, and a gentle heat applied to determine the action. Carbonic acid is then evolved, and escapes through the chloride of calcium tube. To expel the last portions of carbonic acid, the liquid must be ultimately heated till it boils; after which it is left to cool, and weighed: the loss of weight gives the quantity of carbonic acid. Now, as 43·67, the equivalent of bioxide of manganese, is nearly double that of carbonic acid, which is 22, the loss of weight in the apparatus may be taken to represent the quantity of real bioxide in the 50 grains of the sample. [For other methods, see Appendix.]

To obtain a complete appreciation of the value of a sample of manganese, it is not sufficient to know the per-centage of real bioxide in it,—or, which comes to the same thing, the quantity of chlorine it is capable of yielding,—but we must also know the quantity of hydrochloric acid which must be consumed for evolving this chlorine. If the sample consists of pure bioxide, half the acid used will give up its chlorine; if it be pure sesquioxide, only a third of the acid will be changed into chlorine. The quantity of acid required will therefore be greater in the latter case than in the former in the ratio of 3 : 2. Lastly, if the oxide contains lime, baryta, or oxide of iron, these bases will neutralise a portion of the acid without supplying any chlorine. To determine the expenditure of acid, a known weight of the oxide is heated with a known quantity of hydrochloric acid of given strength, the chlorine being suffered to escape, but the hydrochloric acid which would otherwise escape undecomposed being collected in a small receiver moistened on the inside. When the action is over, the acid thus condensed is added to that in the flask, the whole diluted with water, and the quantity of free acid determined by adding a graduated alkaline solution, till the precipitate which forms no longer redissolves on agitation. The quantity of free acid thus determined is then to be deducted from the original quantity, and the difference gives the quantity consumed.

Manganic acid; MnO_3; 51·67 *or* 645·9.—When bioxide of manganese is strongly ignited with hydrate or carbonate of potash in excess, manganic acid is formed, under the influence of the alkali, together with a lower oxide of manganese. Ignition in open vessels, or with an admixture of nitrate of potash, increases the production of the acid, by the absorption of oxygen which then occurs. The product has long been known as *mineral chameleon,* from the property of its solution, which is green at first, to pass rapidly through several shades of colour. But a more convenient process for preparing manganate of potash is that recommended by Dr. Gregory. He mixes intimately 4 parts of bioxide of manganese in fine powder with 3½ parts of chlorate of potash, and adds them to 5 parts of hydrate of potash dissolved in a small quantity of water. The mixture is evaporated to dryness, powdered, and afterwards ignited in a platinum crucible, but not fused, at a low red heat. The ignited mass, digested in a small quantity of cold water, forms a deep green solution of the alkaline manganate, which may be obtained in crystals of the same colour by evaporating the solution over sulphuric acid in the air-pump. Zwenger, by igniting bioxide of manganese with 3 parts of nitric acid, and evaporating the aqueous solution in vacuo, obtained reddish-brown crystals containing $KO.MnO_3$. On exposure to the air, they became dull and dark green. The manganates were discovered by Mitscherlich to be isomorphous with the sulphates and chromates. It has not yet been found possible to isolate manganic acid. Its salts in solution readily undergo decomposition, unless an excess of alkali is present; and are also destroyed by contact of organic matter, such as paper.

Permanganic acid, Mn_2O_7; 111·34 *or* 1391·8.—When the green solution of manganate of potash, prepared as above directed, is diluted with boiling water, hydrated bioxide of manganese subsides, and the liquid assumes a beautiful pink or violet colour. The manganic acid is resolved into bioxide of manganese and hypermanganic acid:

$$3MnO_3 = MnO_2 + Mn_2O_7.$$

The permanganate of potash should be rapidly concentrated, without contact of organic matter, and allowed to crystallize. A better process for obtaining this salt is to mix 1 part of bioxide of manganese, in very fine powder, with 1 part of chlorate of potash; introduce this mixture into a solution of 1¼ part of caustic potash in the smallest possible quantity of water; evaporate to dryness, during which process a considerable quantity of manganate of potash is formed; then heat the mixture slowly to dull redness; boil the product in water; filter through asbestos, and concentrate by evaporation: the liquid, on cooling, deposits permanganate of potash in crystals. It may be purified by solution in a small quantity of boiling water, and recrystallisation. The crystals are of a dark purple colour, almost black, and soluble in sixteen times their weight of cold water; they were found by Mitscherlich to be isomorphous with perchlorate of potash; they dissolve in 16 parts of water at 60° (Regnault). The permanganates give out oxygen when heated, and are reconverted into manganates. Their solutions have a rich purple colour, and are so stable that they may be boiled, if concentrated. A small portion of a permanganate imparts a purple colour to a very large quantity of water.

When a strong solution of caustic potash is added to a dilute solution of permanganate of potash, the liquid changes colour, assuming first a violet, and afterwards an emerald-green tint. The permanganate is in fact converted into manganate, a double quantity of potash having entered into combination with the acid:

$$KO.Mn_2O_7 + KO = 2(KO.MnO_3) + O.$$

The oxygen thus liberated remains dissolved in the water. This transformation is due to the great basic power of the potash. Acids produce the contrary effect, that is to say, they convert manganates into permanganates.

The insoluble manganate of baryta may be formed by fusing bioxide of manganese with nitrate of baryta; and when mixed with a little water, and decomposed by an equivalent quantity of sulphuric acid, affords free permanganic acid. In Mitscherlich's experiments, the free acid appeared to be a body not more stable than bioxide of hydrogen, being decomposed between 86° and 104°, with escape of oxygen gas and precipitation of hydrated bioxide of manganese. It bleached powerfully, and was rapidly destroyed by all kinds of organic matter. M. Hünefeld, on the other hand, obtained permanganic acid in a state in which it could be preserved, evaporated, redissolved, &c. He washed the manganate of baryta with hot water, by which it is resolved into bioxide of manganese and permanganate of baryta, and then added to it the quantity of phosphoric acid exactly necessary to neutralise the baryta. The liberated permanganic acid was dissolved out, evaporated to dryness, and by a second solution and evaporation, obtained in the form of a reddish-brown mass, crystalline and radiated, which exhibited the lustre of indigo at some points and was entirely soluble in water. When dry permanganic acid was fused in a retort with anhydrous sulphuric acid, and afterwards distilled at a higher temperature, an acicular sublimate of a crimson red colour was obtained, which appeared to be a combination of permanganic and sulphuric acids. (Berzelius's *Traité*, i. 522.) When monohydrated sulphuric acid is poured upon a somewhat considerable quantity of crystallised permanganate of potash, the salt is decomposed with great evolution of heat, red flames bursting out, oxygen being evolved, and manganic oxide set free in dark-brown flakes and shreds like spider-lines. The red flames seem to show that permanganic acid is gaseous at the high temperature produced by the reaction. (Wöhler.)

Perchloride of manganese, Mn_2Cl_7, is a greenish yellow gas, which condenses at 0° F. into a liquid of a greenish-brown colour. This liquid diffuses purple fumes, owing to the formation of hydrochloric and permanganic acids, by the decomposition of the moisture of the air. It was formed by Dumas by dissolving manganate of potash in oil of vitriol, pouring the solution into a tubulated retort, and adding by degrees small portions of chloride of sodium or potassium, completely freed from water by fusion. The perchloride of manganese is the result of a reaction between the liberated hypermanganic and hydrochloric acids:

$$Mn_2O_7 + 7HCl = Mn_2Cl_7 + 7HO.$$

A corresponding *perfluoride of manganese* was formed by Wöhler by distilling, in a platinum retort, a mixture of manganate of potash and fluor-spar in powder, with fuming sulphuric acid. It is a greenish-yellow gas, which likewise produces purple fumes in damp air.

Isomorphous relations of manganese. — There is no other element whose compounds enter into so many isomorphous groups, and connect so large a proportion of the elements by the tie of isomorphism, as manganese. The salts of its protoxide are strictly isomorphous with the salts of magnesia and its class; so that manganese belongs to and represents the magnesian family of elements. The same metal connects the sulphur family with the magnesian, by the isomorphism of the sulphates and manganates; and, therefore, sulphur, selenium, and tellurium are thus allied to the magnesian metals. An equally interesting relation is that of permanganic with perchloric acid, and the isomorphism, which it establishes, of 2 equivalents of manganese with 1 equivalent of chlorine, and the other members of its family.

ESTIMATION OF MANGANESE, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

The usual method of precipitating manganese from the solution of a manganous salt, is to add carbonate of soda at a boiling heat. The precipitated carbonate of manganese is then well washed with boiling water, and calcined at a strong red heat, whereby it is converted into manganoso-manganic oxide, Mn_3O_4, containing 72·11 per cent. of manganese. If the solution contains a considerable quantity of ammoniacal salts, it must be evaporated after mixing it with excess of carbonate of soda, and the soluble salts dissolved out of the residue by water.

Manganese is separated from the alkali-metals by means of carbonate of soda or sulphide of ammonium, which latter precipitates it in the form of sulphide. The sulphide is washed with water containing a small quantity of sulphide of ammonium; then redissolved in acid; and the manganese precipitated from the solution by carbonate of soda.

From barium and strontium, manganese is easily separated by means of sulphate of soda, which throws down the baryta and strontia as sulphates; also by sulphide of ammonium. From lime and manganese it is separated by sulphide of ammonium, which, if the solution be sufficiently dilute, precipitates the manganese alone in the form of sulphide. The separation from lime may also be effected by means of oxalate of ammonia, after the addition of chloride of ammonium to keep the manganese in solution.

From alumina and glucina, manganese, if in small or moderate quantity only, may be separated by boiling the solution with potash in an open vessel. The manganese is then precipitated in the form of sesquioxide, while the alumina and glucina are dissolved by the potash. If, however, the proportion of manganese be considerable, this method cannot be used, because the oxide of manganese carries down with it considerable quantities of alumina and glucina. In this case, the liquid must be mixed with sal-ammoniac and the alumina and glucina precipitated by ammonia. The precipitate, however, always contains small quantities of manganese, which must be separated by subsequent treatment with potash.

SECTION II.

IRON.

Eq. 28 *or* 350; Fe (*ferrum*).

The most remarkable of the metals; the production of which, from the numerous and important applications it possesses, appears to be an indispensable condition of civilisation. Meteoric masses of iron, often so pure as to be malleable, are found widely although thinly scattered over the earth's surface, and probably first attracted the attention of mankind to this metal. Of the occurrence of metallic iron as a terrestrial mineral *in situ*, the best established instances are the species of native iron which accompanies the Uralian platinum, and a thin vein about two inches in thickness, observed in chlorite slate, near Canaan in the United States. In a state of combination, iron is extensively diffused, being found in small quantity in the soil, and in most minerals, and as sulphide, oxide, and carbonate, in quantities which afford an inexhaustible supply of the metal and its preparations, for economical purposes.

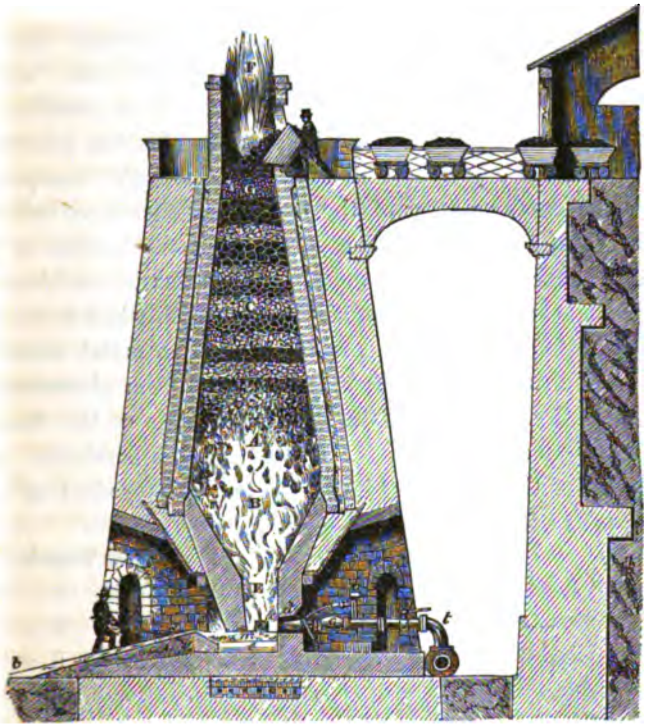
Iron differs from all other metals in two points, which greatly affect the methods of reducing it. Its particles agglutinate at a full red heat, although the pure metal is nearly infusible. The oxides of iron, which are easily reduced by combustible matter, thus yield in the furnace a spongy metallic mass, which may admit of being compacted by subsequent heating and hammering, if the oxide has originally been free from earthy and other foreign matter. Such probably was everywhere the earliest mode of treating the ores of iron, and we find it still followed among rude nations. But iron is also singular in forming, at an elevated temperature, a fusible compound with carbon (cast iron), the production of which facilitates the separation of the metal from every thing extraneous in the ore, and is the basis of the only method of extracting iron extensively practised.

The ore of iron most abundant in the primary formations is the black oxide or *magnetic ore*, which affords the most celebrated and valuable irons of Sweden and the north of Europe, but of which the application is greatly circumscribed from its not being associated with coal. In the secondary and tertiary formations, the anhydrous and hydrated sesquioxide of iron, *red* and *brown hematite*, occur occasionally in considerable quantity, often massive, reniform, and quite pure, at other times pulverulent and mixed with clay. It is employed to some extent in England in the last condition, but only for the purpose of mixing with the more common ore. The crystallised carbonate of iron, or *spathic iron*, is smelted in some parts of the continent, and gives an iron often remarkable for a large proportion of manganese. The celebrated iron of Elba is derived from *specular* or *oligistic iron*, a crystallised sesquioxide. But the consumption of all these ores is inconsiderable, compared with that of the *clay ironstone* of the coal measures. This is the carbonate of the protoxide of iron mixed with variable quantities of clay and carbonates of lime, magnesia, &c.; it is often called the argillaceous carbonate of iron. It is a sedimentary rock wholly without crystallisation, resembling a dark-coloured limestone, but of higher density, from 2·936 to 3·471, and not effervescing so strongly in an acid. It occurs in strata, beds, or bands, as they are also named, from 2 to 10 or 14 inches in thickness, alternating with beds of coal, clay, bituminous schist, and often limestone. The proportion of iron in this ore varies considerably, but averages about 30 per cent., and after it has been calcined, to expel carbonic acid and water, about 40 per cent.*

SMELTING CLAY IRON-STONE.

The blast furnace, in which the ore is reduced, is of the form represented below, 40 to 65 feet in height, with

Fig. 2.



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* Accurate analyses of several Scotch varieties of this ore have been published by Dr. H. Colquhoun (Brewster's *Journal*, vii. 234; or Dr. Thomson's *Outlines of Mineralogy and Geology*, i. 446); and of the French ores, by

an interior diameter of from 14 to 17 feet at the widest part. The cavity of the furnace is entirely filled with fuel and the other materials, which are continuously supplied from an opening near the top; and the combustion maintained by air thrown in at two or more openings, called tuyeres, near the bottom, under a pressure of about 6 inches of mercury, from a blowing apparatus, so as to maintain the whole contents of the furnace in a state of intense ignition. When the air to support the combustion has attained a temperature of 600° or 700°, by passing through heated iron tubes, before it is thrown into the furnace, raw coal may be used as the fuel; but with cold air, the coal must be previously charred to expel its volatile matter, and converted into coke, otherwise the heat produced by its combustion is insufficient. With the ore and fuel, a third substance is added, generally limestone, the object of which is to form a fusible compound with the earthy matter of the ore; it is, therefore, called a *flux*. Two liquid products accumulate at the bottom of the furnace, namely, a glass composed of the flux in combination with the earthy impurities of the ore, which when drawn off forms a solid *slag*, and the carbide of iron, or metal, which is the heavier of the two. It may be drawn from observations made by Dr. Clark, in 1833, on the working of the Scotch blast furnaces, under the *hot blast*, that the relative proportions of the materials, including air, and product of cast iron, are as follows*:—

	Weight.
Coal	5
Roasted iron-stone	5
Limestone	1
Air	11
Average product of cast iron . .	2

M. Berthier, in his *Traité des essais par la voie sèche*, ii. 252, a work which is invaluable for the metallurgic student, and Mitchell's *Practical Assaying*, 8vo.

* Edinburgh Phil. Trans. vol. 18.

The ultimate fixed products are the slag and carburet of iron, but the formation of these is preceded by several interesting changes which the ore successively undergoes in the course of its descent in the furnace. A portion of the oxide of iron is certainly reduced to the metallic state, soon after its introduction, in the upper part of the furnace, by carbonic oxide and volatile combustible matter; but the reduced metal does not then fuse. A large portion of the oxide of iron must combine also, at the same time, with the silica and alumina present in the ore, which act as acids, and a glass be formed, the oxide of iron in which is scarcely reducible by carbon. But this injurious effect of the acid earths is counteracted by the lime of the flux, which, being a more powerful base than oxide of iron, liberates that oxide from the glass when the proportions of the materials introduced into the furnace are properly adjusted, and neutralises the silica; so that the slag eventually becomes a silicate of lime and alumina, with scarcely a trace of oxide of iron. The whole oxide of iron comes thus to be exposed to the reducing action of the volatile combustible, and consequently the whole iron is probably, at one time, in the condition of pure or malleable iron. But when the metal descends somewhat farther in the furnace, it attains the high temperature at which it combines with the carbon of the coke in contact with it, and it fuses for the first time, in the form of carburet of iron. It has not yet, however, attained its ultimate condition. When it reaches, in its descent, the region of the furnace where the heat is most intense, its carbon reacts on the silica, alumina, lime, and other alkaline oxides contained in the fluid slag with which it is accompanied, reducing portions of silicon, aluminum, calcium, and other alkaline metals, which combine with the iron. The proportion of carbon replaced by silicon and metallic bases is generally found to be greater in iron prepared by the hot than by the cold blast, owing, it is presumed, to the higher temperature of the furnace with the hot blast.

The introduction of air already heated to support the combustion of the blast furnace, for which a patent was obtained by Mr. J. B. Neilson, has greatly reduced the proportion of coal required to smelt a given weight of ore, enabling the iron-master, indeed, to effect a saving of more than three-fourths of the coal where it is of a bituminous quality. The air is heated between the blowing apparatus and the furnace, by being made to circulate through a set of arched tubes of moderate diameter, heated by a fire beneath them. The air can be heated in this manner to low redness, or to near 1000°, but there is found to be no proportional advantage in raising its temperature much above the melting point of lead (612°), which is already higher than the point at which charcoal inflames. Considering the great weight of air that enters the furnace, the temperature of that material must greatly affect the whole temperature of the furnace, particularly of the lower part, where the air is admitted, and which part it is desirable should be hottest. Now a certain elevated temperature is required for the proper smelting of the ore, and, unless attained in the furnace, the fuel is consumed to no purpose. The removal of the negative influence of the low temperature of the air, appears to permit the heat to rise to the proper point, which otherwise is attained with difficulty and by a wasteful consumption of fuel. Professor Reich, of Freiberg, has observed that heating the air likewise alters the relative temperatures of different parts of the furnace, depressing in particular, and bringing nearer the tuyeres, the zone of highest temperature. The admixture of steam with the air has, he finds, precisely the opposite effect, elevating the zone of highest temperature in the furnace; so that the effect of the hot blast may be exactly neutralised by mixing steam with the hot air.

Cast iron.—The fused metal is run into channels formed in sand, and thus cast into ingots or pigs, as they are called.

Cast iron is an exceedingly variable mixture of reduced substances, of which the principal is iron combined with carbon. The theoretical constitution to which that variety of it, most definite in its composition, approaches, is the following:—

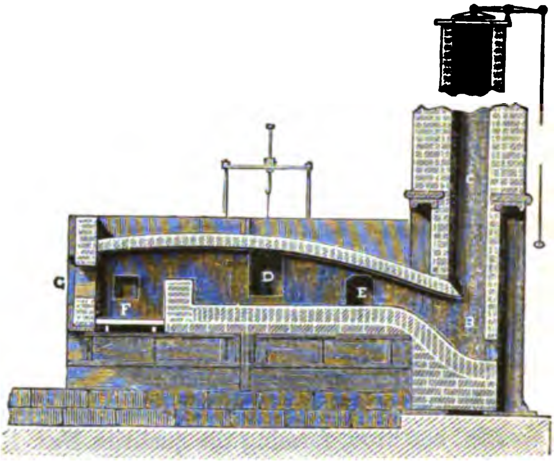
WHITE CAST IRON.

4 equivalents of iron . . .	94·9
1 equivalent of carbon . .	5·1
	100·0

The difference in appearance and quality of the varieties of cast iron is not well accounted for by their composition. The grey or mottled cast iron, forming the qualities Nos. 1 and 2, presents a fracture composed of small crystals, is easily cut by the file, and is preferred for castings. It is generally supposed that a portion of uncombined carbon is diffused through the iron of these qualities, in the form of graphite. No. 3, or white cast iron, is more homogeneous; its fracture exhibits crystalline plates, like that of antimony, and is nearly white; it is exceedingly hard and brittle.

Malleable iron.—The great proportion of cast iron manufactured is afterwards refined, or converted into bar or malleable iron. The mode of effecting this conversion varies with the nature of the fuel. Where coal or coke is used, as in this country, the process consists of two stages. In the first, which is called *refining,* the pig-iron is heated in contact with the fuel in small low furnaces called *refineries,* while air is blown over its surface by means of tuyeres. The effect of this operation is to deprive the iron of a great portion of the carbon and nearly all the silicon associated with it. The metal thus far purified is run out into a trench, and suddenly cooled by pouring cold water upon it. It then forms a greyish-white very brittle mass, blistered on the surface. In

Fig. 3.



this state it is called *fine metal.* It is then ready for the second and principal operation, called the *puddling* process, which consists in heating masses of the iron with a certain access of air in a kind of reverberatory furnace, called the *puddling furnace,* of which Fig. 3. represents a vertical section. This furnace has four doors, two of which, *F* and *G,* serve for the introduction of fuel to the grate; the charge of metal is introduced at *E;* and *D* serves for the insertion of a long poker or spatula, with which the metal is stirred about. The hearth of the furnace has an aperture *B* at the back, for removing the slag. The furnace having been brought to a bright red heat, about four or five hundred-weight of fine metal is introduced, together with one hundred-weight of rich scoriæ or forge cinders (scale-oxide). The metal then fuses, and in this state the workman stirs it about with the poker, so as to expose every part to the flame. The carbon is thus gradually burnt out, partly by the direct action of oxygen in the flame, and partly by cementation with the oxide of iron; and the metal becomes less fusible, and thick and tenacious, so that it sticks together, and is easily formed into four or five large balls, called blooms. In this condition it is removed by tongs, compressed into a cylindrical form by a few blows of a loaded hammer, and quickly converted into a bar, by pressing it between grooved rollers. The tenacity of the metal is further increased by welding several bars together; a faggot of bars is brought to a white heat in an oblong furnace, and then extended between the grooved rollers into a single bar.

The texture of malleable iron is fibrous. Although the purest commercial form of the metal, it still contains about one-half per cent. of carbon, with traces of silicon and other metals.

Pure iron may, however, be obtained by introducing into a Hessian crucible 4 parts of iron wire cut into small pieces, and 1 part of black oxide of iron; placing above these a mixture of white sand, lime, and carbonate of potash, in the proportions used for glass-making; covering the crucible with a closely fitting lid; and exposing it to a very high temperature. A button of pure metal is thus obtained, the traces of carbon and silicon in the iron having been removed by the oxygen of the oxide. (Mitscherlich.)

Steel.—Only the best qualities of malleable iron, those prepared from a pure ore, and reduced by means of charcoal, such as the Swedish iron, are converted into steel. An iron box is filled with flat bars of such iron and charcoal powder, in alternate layers, and kept at a red heat for forty-eight hours, or longer. The surface of the bars is found afterwards to be blistered, and they have absorbed from 1·3 to 1·75 per cent. of carbon. This is the process of cementation. It is known that iron can be converted into steel without being in actual contact with charcoal, provided the iron and charcoal are in a close vessel together, and oxygen be present, the carbon reaching the surface of the metal in the form of carbonic oxide gas. The iron becomes harder by this change, and more fusible, but can still be hammered into shape, and cut with a file. The property in which steel differs most from soft iron, is the capacity it has acquired of becoming excessively hard and elastic, when heated to redness and suddenly cooled by plunging it into cold water or oil. This hardness makes steel invaluable for files, knives, and all kinds of cutting instruments. But the steel, when hardened in the manner described, is harder than is required for most of its applications, and also very brittle. Any portion of its original softness can be restored to the steel by heating it up to particular temperatures,—which are judged of by the colour of the film of oxide upon its surface, which passes from pale yellow at about 430°, through straw yellow, brown yellow, and red purple into a deep blue at 580°,—and allowing the steel afterwards to cool slowly. Articles of steel are *tempered* in this manner.

A simple and expeditious method of converting crude or pig-iron into malleable iron and steel, *without the aid of fuel*, has lately been proposed by Mr. H. Bessemer. This process consists in causing cold air to bubble through the liquid iron; under which circumstances the oxygen of the air combines with the carbon of the iron, removing it in the form of carbonic oxide, and generating sufficient heat to keep the iron in the liquid state without external heating, and to sustain the action till the whole, or any required proportion, of the carbon is burnt away. As the quantity of carbon in the metal diminishes, part of the oxygen combines with the iron, converting it into an oxide, which, at the very high temperature then existing in the vessel, melts, and forms a powerful solvent for the earthy bases associated with the iron. At a certain stage of the process, the whole of the crude iron is said to be converted into cast steel of ordinary quality. By continuing the process, the steel thus formed is gradually deprived of its small remaining portion of carbon, and passes successively from hard to soft steel, steely iron, and ultimately to very soft iron.*

Properties of iron.—Iron is of a bluish-white colour, and admits of a high polish. It is remarkably malleable, particularly at a high temperature, and of great tenacity. Its mean density is 7·7, which is increased by fusion to 7·8439. When kept for a considerable time at a red heat, its particles often form large cubic or octohedral crystals, and the metal becomes brittle. Malleable iron softens before entering into fusion, and in this state it can be *welded*, or two pieces united by hammering them together. The point of fusion of cast iron is 3479°; that of malleable iron is much higher. Cast-iron expands in becoming solid, and therefore takes the impression of a mould with exactness. Iron is attracted by the magnet at all temperatures under an orange-red heat. It is then itself magnetic by induction, but immediately loses its polarity, if pure, when withdrawn from the magnet. If it contains carbon, as steel and cast iron, it is affected less strongly, but more durably, by the proximity of a magnet, becoming then permanently magnetic. Among the native compounds of iron, the black oxide, which forms the loadstone, and the corresponding sulphide, are those which share this property with the metal in the highest degree. A steel magnet loses its polarity at the boiling point of almond oil; a loadstone, just below visible ignition (Faraday).

Iron reduced from the oxide by hydrogen at a heat under redness, forms a spongy mass, which, when exposed to air, takes fire spontaneously at the usual temperature, oxide of iron being reproduced (Magnus). But iron, in mass, appears to undergo no change in dry air, and to be incapable of decomposing pure water at ordinary temperatures. Nor does it appear to be acted upon by oxygen and water together; but the presence of carbonic acid in the water causes the iron to be rapidly oxidated, with evolution of hydrogen gas. In the ordinary rusting of iron, the carbonate of the protoxide appears to be first produced, but that compound gradually passes into the hydrated sesquioxide, and the carbonic acid is evolved. The rust of iron always contains ammonia, probably absorbed from the air; the native oxides of iron also contain ammonia. Iron remains bright in solutions of the alkalies and in lime-water, which appear to protect it from oxidation; but neutral, and more particularly acid salts, have the opposite effect. The corrosion of iron under water appears, in general, to be immediately occasioned by the formation of a subsalt of that metal with excess of oxide, the acid of which is supplied by the saline matter in solution. Articles of iron may be completely defended from the injury occasioned in this way, by contact with the more positive metal zinc, as in galvanized iron (I., 257), while the protecting metal itself wastes away very slowly. Cast iron is converted into a species of graphite by many years' immersion in sea-water, the greater part of the iron being dissolved while the carbon remains.* In open air, iron burns at a high temperature with vivacity, and its surface becomes covered with a fused oxide, which forms smithy ashes. Iron also decomposes steam at a red heat, and the same oxide is formed as by the combustion of the metal in air, namely, the magnetic or black oxide, $FeO.Fe_2O_3$.

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* Chemical Gazette, 1856. p. 336.

Iron dissolves readily in diluted acids, by substitution for hydrogen, which is evolved as gas. Strong nitric acid acts violently upon iron, yielding oxygen to it, and undergoing decomposition. But the relations of iron to that acid when slightly diluted are exceedingly singular; they have been particularly studied by Professor Schönbein.

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* Mr. Mallet has collected much information respecting the corrosion of iron, in his First Report to the British Association, on the action of sea and river water upon cast and wrought iron, 1839.

Passive condition of iron.—Pure malleable iron, such as a piece of clean stocking wire, usually dissolves in nitric acid of sp. gr. 1·3 to 1·35, with effervescence; but it may be thrown into a condition in which it is said by Schönbein to be *passive*, as it is no longer dissolved by that acid, and may be preserved in it for any length of time without change:—1. By oxidating the extremity of the wire slightly, by holding it for a few seconds in the flame of a lamp, and after it is cool dipping it gradually in the nitric acid, introducing the oxidated end first. 2. By dipping the extremity of the wire once or twice in concentrated nitric acid, and washing it with water. 3. By placing a platinum wire first in the acid, and then introducing the iron wire, preserving it in contact with the former, which may afterwards be withdrawn. 4. A fresh iron wire may be introduced in the same manner into the nitric acid, in contact with a wire already passive; this may render passive a third wire, and so on. 5. By making the wire the positive pole or zincoïd of a voltaic battery, introducing it after the negative pole or chloroïd has been placed in the acid. Oxygen gas is then evolved from the surface of the iron wire, without combining with it, as if the wire were of platinum. As the passive state can be communicated by contact of passive iron, so it may be destroyed by contact with active iron (or zinc) undergoing, at the moment, solution in the acid. If passive iron be made a negative pole (chlorous) in nitric acid, it also ceases to resist solution. The indifference to chemical action exhibited by iron when passive, is not confined to nitric acid of the density mentioned, but extends to various saline solutions which are usually acted upon by iron. An indifference to nitric acid of the same kind can also be acquired by other metals as well as iron, particularly by bismuth (Dr. Andrews), but in a much less degree. To account for this remarkable phenomenon various theories have been proposed. Schönbein and Wetzlar attribute it to a peculiar electro-dynamic condition of the surface of the metal, similar to that of the platinum in Grove's gas battery (I. 268—270). Mousson attributes it to a coating of nitrous acid. By others again it has been ascribed to a peculiar antagonism between two forces acting simultaneously on the metal, the one tending to oxidate it at the expense of the nitric acid, the other to cause it to take the place of hydrogen in the nitrate of water, just as when it dissolves in sulphuric acid.* But perhaps the most probable explanation is that which attributes the passive condition of iron to the formation on its surface of a thin film of anhydrous ferric oxide, similar to specular iron. This view is supported by the fact that iron which has been ignited, and is therefore completely covered with black oxide, exhibits the same characters, excepting that, from the greater thickness of the coating, the passive state is more complete. It may also be observed, that iron becomes passive only in liquids which give up oxygen, and that in the voltaic circuit it becomes passive precisely under the circumstances in which it is exposed to oxidation, *i. e.* when it is made the zincoid or positive pole, and that it becomes active again when made the negative pole, that is to say, when the oxide is reduced. The same view is supported by the observation that iron rendered passive in nitric acid immediately begins to dissolve on the addition of hydrochloric acid.

PROTOCOMPOUNDS OF IRON; FERROUS COMPOUNDS.

Protoxide of iron, Ferrous oxide; FeO; 36 *or* 450. — Iron appears to admit of three degrees of oxidation, the protoxide and sesquioxide, which are both basic and correspond respectively with manganous and manganic oxide, and ferric acid. The protoxide is not easily obtained in a dry state, from the avidity with which it absorbs oxygen. The purest anhydrous protoxide is obtained by igniting the oxalate out of contact of air; but even this, according to Liebig, contains a small quantity of metallic iron. The protoxide exists in the sulphate and other salts of iron, formed when the metal dissolves in an acid with evolution of hydrogen.

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* Dr. Andrews indeed concludes from observation, that the ordinary chemical action of a hydrated acid upon the metals which dissolve in it, is in general diminished, when the acid is concentrated, by the voltaic association of these metals with such metals as gold, platinum, &c.; while, on the contrary, it is increased when the acid is diluted.—Trans. of the Royal Irish Academy, 1838; or, Becquerel, vol. v. pt. 2, p. 187.

Solutions of ferrous salts have a green colour. *Potash* or *soda* added to them throws down the protoxide as a white hydrate, which becomes black on boiling, from loss of water. The colour of the white precipitate changes by exposure to air, to grey, then to green, bluish black, and finally to an ochrey red, when it is entirely sesquioxide. *Ammonia* exercises a similar action, but does not precipitate the whole of the oxide, because the precipitate dissolves in the ammoniacal salt produced. *Alkaline carbonates* form a precipitate of carbonate of iron, which is white at first, but soon becomes of a dirty green, and undergoes the same subsequent changes from oxidation. Ferrous salts are not precipitated by *hydrosulphuric acid,* the sulphide of iron being dissolved by strong acids, but give a black sulphide with solutions of *alkaline sulphides.* They give a white precipitate with *ferrocyanide of potassium,* which gradually becomes of a deep blue when exposed to air; with the *ferricyanide,* a precipitate which is at once of an intense blue, being one of the varieties of prussian blue. The infusion of *gall-nuts* does not affect a solution of the protoxide of iron when completely free from sesquioxide.

Protosulphide of iron is prepared by heating to redness, in a covered crucible, a mixture of iron filings and crude sulphur, in the proportion of 7 of the former to 4 of the latter. It dissolves in sulphuric and hydrochloric acids, with evolution of hydrosulphuric acid gas (I. 420.).

A *subsulphide of iron,* Fe_2S, appears to be formed when the sulphate of iron is reduced by hydrogen, one-half of the sulphur coming off in the form of sulphurous acid. This subsulphide is analogous to the subsulphides of copper and lead, which crystallise in octahedrons.

Protochloride of iron crystallises with 4HO, and is very soluble. Like all soluble ferrous salts, it is of a green colour, gives a green solution, and has a great avidity for oxygen.

Protiodide of iron is formed when iodine is digested with water and iron wire, the latter being in excess, and is obtained as a crystalline mass by evaporating to dryness. It was introduced into medical use by Dr. A. T. Thomson. A piece of iron wire is placed in the solution of this salt to preserve it from oxidising. The protiodide of iron dissolves a large quantity of iodine, without becoming periodide, as the excess of iodine may be precipitated by starch.

Protocyanide of iron C_2NFe or FeCy, is as difficult to obtain as the protoxide of iron. When cyanide of potassium is added to a protosalt of iron, a yellowish-red precipitate appears, which dissolves in an excess of the alkaline cyanide, and forms the ferrocyanide of potassium (I., 529.). A grey powder remains on distilling the ferrocyanide of ammonium at a gentle heat; and a white insoluble substance on digesting recently precipitated prussian blue in sulphuretted hydrogen water, contained in a well-stopped phial; these products, although they differ considerably in properties, have both been looked upon as protocyanide of iron. This compound is also obtained as a white deposit on boiling an aqueous solution of hydroferrocyanic acid, H_2FeCy_3. The same solution heated with red oxide of mercury forms cyanide of mercury and white protocyanide of iron. The most remarkable property of this cyanide is its tendency to combine with other cyanides of all classes, and to form double cyanides, or to enter as a constituent into the salt-radicals ferrocyanogen and ferricyanogen, Cy_3Fe and Cy_6Fe_2.

Hydroferrocyanic acid; H_2FeCy_3 or $2HCy,FeCy$. This compound was discovered by Mr. Porrett. It may be obtained by decomposing ferrocyanide of barium with sulphuric acid, or ferrocyanide of potassium with an alcoholic solution of tartaric acid, or ferrocyanide of lead with hydrosulphuric acid. It is soluble in water and alcohol, insoluble in ether, and crystallises by spontaneous evaporation in cubes or four-sided prisms, or sometimes in tetrahedrons. When dry, it may be kept for a long time without alteration in close vessels; but is decomposed on exposure to the air with evolution of hydrocyanic acid, and formation of prussian blue.

Hydroferrocyanic acid unites with most salifiable bases, forming the salts called *ferrocyanides,* whose general formula is M_2FeCy_3, the symbol M denoting a metal. The ferrocyanides of ammonium, potassium, sodium, barium, strontium, calcium, and magnesium, dissolve readily in water; the rest are insoluble or sparingly soluble. Some of them, as the copper and uranium salts, are very highly coloured. Ferrocyanide of potassium has been already described (I. 529.).

Ferrocyanide of potassium and iron; $KFe_2Cy_3 = (KFe), (Cy_3Fe)$.—The bluish-white precipitate which falls on testing a protosalt of iron with the ferrocyanide of potassium or yellow prussiate of potash, *e.g.*, with the protochloride:

$$K_2FeCy_3 + FeCl = KCl + KFe_2Cy_3.$$

It is also obtained in the form of a white crystalline salt (mixed with bisulphate of potash), in the preparation of hydrocyanic acid, by distilling ferrocyanide of potassium with dilute sulphuric acid:

$$2K_2FeCy_3 + 6SO_3 + 6HO = 3(KO,HO,2SO_3) + 3HCy + KFe_2Cy_3.$$

Exposed to the air, it absorbs oxygen and becomes blue. It then affords ferrocyanide of potassium to water, and after all soluble salts are removed, a compound remains, which Liebig names the *basic sesquiferrocyanide of iron,* and represents by the formula $Fe_4.3(Cy_3Fe) + Fe_2O_3$, corresponding, as will be seen hereafter, with 1 eq. of prussian blue + 1 eq. of sesquioxide of iron. This basic compound is dissolved entirely by continued washing, and affords a beautiful deep blue solution. The addition of any salt causes the separation of this compound. Its solution may be evaporated to dryness without decomposition. The white ferrocyanide of iron and potassium likewise turns blue when treated with chlorine-water or nitric acid, being thereby converted into ferricyanide of iron and potassium (KFe_4Cy_6).

$$2KFe_2Cy_3 + Cl = KFe_4Cy_6 + KCl.$$

This latter compound, which when dry is of a beautiful violet colour, may be regarded as ferricyanide of potassium $K_3Fe_2Cy_6$, in which 2 eq. of potassium are replaced by iron (Williamson).

Ferricyanide of iron, Turnbull's blue; $Fe_3(Cy_6Fe_2)$.—This is the beautiful blue precipitate which falls on adding the ferricyanide of potassium (red prussiate of potash) to a protosalt of iron. It is formed by the substitution of 3 eq. of iron for the 3 eq. of potassium of the latter salt (I. 530). The same blue precipitate may be obtained by adding to a protosalt of iron a mixture of yellow prussiate of potash, chloride of soda, and hydrochloric acid. The tint of this blue is lighter and more delicate than that of prussian blue. It is occasionally used by the calico-printer, who mixes it with permuriate of tin, and prints the mixture, which is in a great measure soluble, upon Turkey-red cloth, *raising* the blue colour afterwards by passing the cloth through a solution of chloride of lime containing an excess of lime. The chief object of that operation is indeed different, namely, to discharge the red and produce white patterns, where tartaric acid is printed upon the cloth; but it has also the effect incidentally of precipitating the blue pigment and peroxide of tin together on the cloth, by neutralising the acid of the premuriate of tin. This blue is believed to resist the action of alkalies longer than ordinary prussian blue. It is distinguished from prussian blue by yielding, when treated with caustic potash or carbonate of potash, a solution of ferrocyanide of potassium, and a residue of ferroso-ferric oxide:

$$3Fe_5Cy_6 + 4KO = 2K_2FeCy_3 + Fe_3O_4;$$

whereas prussian blue treated in the same manner yields ferric oxide (Williamson).

Carbonate of iron is obtained on adding carbonate of soda to the protosulphate of iron, as a white or greenish-white precipitate, which may be washed and preserved in a humid condition in a close vessel, but cannot be dried without losing carbonic acid and becoming sesquioxide of iron. It is soluble, like the carbonate of lime, in carbonic acid water, and exists under that form in most natural chalybeates. Carbonate of iron occurs also crystallised in the rhombohedral form of calc-spar, forming the mineral *spathic iron*, which generally contains portions of the carbonates of lime, magnesia, and manganese. It is generally of a cream colour or black, and its density rarely exceeds 3·8. This anhydrous carbonate does not absorb oxygen from the air. Carbonate of iron is also the basis of clay iron-stone. There is no carbonate of the sesquioxide.

Protosulphate of iron, Ferrous sulphate, Green vitriol, Copperas; $FeO.SO_3, HO + 6HO$; 76 + 63 *or* 950 + 787·5.—This salt may be formed by dissolving iron in sulphuric acid diluted with 4 or 5 times its bulk of water, filtering the solution while hot, and setting it aside to crystallise. But the large quantities of sulphate of iron consumed in the arts are prepared simultaneously with alum, by the oxidation of iron pyrites (I. 606).

The commercial salt forms large crystals, derived from an oblique rhomboïdal prism, which effloresce slightly in dry air, and, when at all damp, absorb oxygen and become of a rusty red colour; hence the origin of the French term *couperose* applied to this salt, and corrupted in our language into copperas. If these crystals be crushed and deprived of all hygrometric moisture by strong pressure between folds of cotton cloth or filter paper, they may afterwards be preserved in a bottle without any change from oxidation. Of the $7HO$ which sulphate of iron contains, it loses $6HO$ at 238°, but retains 1 eq. even at 535°. It may, however, be rendered perfectly anhydrous, with proper caution, without any appreciable loss of acid. The anhydrous salt is also obtained in very small crystalline scales by immersing the hydrated crystals in strong boiling sulphuric acid, and leaving the liquid to cool. The salt was observed by Mitscherlich to crystallise at 176°, with $4HO$, in a right rhombic prism, like the corresponding sulphate of manganese. When its solution containing an excess of acid is evaporated by heat, a saline crust is deposited, which, according to Kuhn, contains $3HO$. The sulphate of iron appears to form neither acid nor basic salts. One part of copperas requires to dissolve it, the following quantities of water, at the particular temperatures indicated above each quantity, according to the observations of Brandes and Firnhaber:—

50°	59°	75·2°	109·4°	114·°	140·0°	183·2°	194°	212°
1·64	1·43	0·87	0·66	0·44	0·38	0·37	0·27	0·30

Ferrous sulphate undergoes decomposition at a red heat, changing into ferric sulphate, and leaves, after all the acid is expelled, the red sesquioxide known as colcothar. This sulphate, like all the magnesian sulphates, forms with sulphate of potash a double salt containing $6HO$. A solution of the sulphate of iron absorbs nitric oxide, and becomes quite black; according to Peligot, it takes up the gas in the proportion of 9 parts to 100 anhydrous salt, or one-fourth of an equivalent (I., 342).

Protonitrate of iron, Ferrous nitrate, may be formed by dissolving the protosulphide in cold dilute nitric acid; the solution evaporated in vacuo yields pale green, very soluble crystals. The solution of the neutral salt is decomposed near the boiling heat, with evolution of nitric acid and copious precipitation of a ferric subnitrate. Iron turnings dissolve in dilute nitric acid and form the same salt, without evolution of gas, the water and acid being decomposed in such a manner as to form ammonia, at the same time that they oxidate the iron.

Protoacetate of iron, Ferrous acetate, is obtained by dissolving the metal or its sulphide in acetic acid. It forms small green prisms which decompose very readily in the air.

Tartrate of potash and iron, Potassio-ferrous tartrate, is prepared by boiling bitartrate of potash with half its weight of iron turnings and a small quantity of water. Hydrogen is evolved, and a white, granular, sparingly soluble salt formed which blackens in the air from absorption of oxygen. It is used medicinally. The iron of this salt is not precipitated by hydrate or carbonate of potash.

SESQUICOMPOUNDS OF IRON; FERRIC COMPOUNDS.

Sesquioxide of iron; Peroxide of iron; Ferric oxide, 80 or 1000.—Occurs very abundantly in nature: 1. as *oligistic* or *specular iron,* in crystals derived from a rhombohedron very near the cube, which are of a brilliant metallic black and highly iridescent. Their powder is red; their density, from 5·01 to 5·22. This oxide forms the celebrated Elba ore.—2. As *red hematite,* in fibrous, mammillated, or kidney-shaped masses, of a dull red colour, very hard, and of sp. gr. from 4·8 to 5·0. This mineral when cut forms the burnishers of bloodstone.—3. also in combination with water, as *brown hematite,* which is much more abundantly diffused than the anhydrous sesquioxide, the granular variety supplying, according to M.

Berthier, more than three-fourths of the iron-furnaces in France. Its density is 3·922; its powder is brown with a shade of yellow, and it dissolves readily in acid, which the anhydrous sesquioxide does not. From analyses by Dr. Thomson and M. Berthier, this mineral appears to unite with 1 eq. of water, as $HO.Fe_2O_3$, analogous to the magnetic oxide of iron, $FeO.Fe_2O_3$. The hydrated sesquioxide produced by the oxidation of iron pyrites, of which it retains the form, contains 1 eq. of water, or 10·31 per cent., and that from the oxidation of the carbonate of iron, 3 eq. of water, or 14·71 per cent., to 2 eq. of sesquioxide (Mitscherlich, *Lehrbuch*, II. 23, 1840). The hydrate is the yellow colouring matter of clay, and with silica and clay it forms the several varieties of ochre.

When metallic iron is oxidated gradually in a large quantity of water, there forms around it a light precipitate of a bright orange yellow colour, which, according to Berzelius, is a ferric hydrate, and of which the empirical formula is $2Fe_2O_3+3HO$, the usual composition of brown hematite. When iron is oxidated in deep water, it is converted, according to E. Davy, into the magnetic oxide, which is possibly formed by cementation from the hydrated sesquioxide. The hydrated sesquioxide is also obtained, by precipitation from ferric salts, by ammonia and by hydrated or carbonated alkali; but never pure, as when an insufficient quantity of alkali is added, a subsalt containing acid is precipitated; and when the alkali is added in excess, a portion of it goes down in combination with the oxide, and cannot be entirely removed by washing. When ammonia is used, the water and excess of the precipitant may be expelled by ignition, and the pure sesquioxide obtained. The latter is not magnetic, and after ignition dissolves with difficulty in acids. When ignited strongly, it loses oxygen and becomes magnetic.

Ferric oxide and its compounds are strictly isomorphous with alumina and the compounds of that earth, and remarkably analogous to them in properties. It is a weak base, of which the salts have a strong acid reaction, and are decomposed by all the magnesian carbonates, as well as by the magnesian oxides themselves. The solutions of its salts, which are neutral in composition, have generally a yellow tint; but they are all capable, when rather concentrated, of dissolving a great excess of ferric oxide, and then become red. Very dilute solutions of the neutral salts of ferric oxide are decomposed by ebullition, and the oxide entirely precipitated, the acid of the salt then uniting with water as a base (Scheerer).

Iron is most conveniently distinguished by tests, or precipitated for quantitative estimation, when in the state of sesquioxide. The solution of a ferrous salt is usually oxidised by transmitting a current of chlorine through it, or by adding to it, at the boiling point, nitric acid, in small quantities, so long as effervescence is occasioned from the escape of nitric oxide. *Alkalies* and *alkaline carbonates* throw down a red-brown precipitate of hydrated sesquioxide. *Hydrosulphuric acid* converts a sesquisalt of iron into a protosalt, with precipitation of sulphur. *Ferrocyanide of potassium* throws down prussian blue, but the ferricyanide has no effect upon ferric salts beyond slightly changing the colour of the solution. *Sulphocyanide of potassium* produces a deep wine-red solution with ferric salts, which becomes perfectly colourless when considerably diluted with water, provided the iron salt is not in great excess. *Infusion of gall-nuts* produces a bluish-black precipitate — the basis of common writing ink.

A remarkable insoluble modification of the hydrated sesquioxide is produced by boiling the ordinary hydrate (precipitated from the chloride by ammonia) in water for 7 or 8 hours. The colour then changes from ochre-yellow to brick-red, and the hydrate thus altered is scarcely acted upon by strong boiling nitric acid, and but very slowly by hydrochloric acid. In acetic acid, or dilute nitric or hydrochloric acid, it dissolves, forming a red liquid, which is clear by transmitted but turbid by reflected light; is precipitated by the smallest quantity of an alkali-salt or a sulphate; and on addition of strong nitric or hydrochloric acid, yields a red granular precipitate which re-dissolves on diluting the liquid with water. The modified hydrate does not form prussian blue with ferrocyanide of potassium and acetic acid. It appears to be $Fe_2O_3.HO$, the ordinary precipitated hydrate, after drying in vacuo, being $2Fe_2O_3.3HO$. This insoluble hydrate is likewise precipitated when a solution of the ordinary hydrate in acetic acid is rapidly boiled. The same solution, if kept for some time at 212° in a close vessel, becomes light in colour, no longer forms prussian blue with ferrocyanide of potassium, or exhibits any deepening of colour on addition of a sulphocyanide; strong hydrochloric or nitric acid, or a trace of an alkali-salt, or sulphuric acid, throws down all the ferric oxide in the form of the insoluble hydrate.* It has also been observed that ferric hydrate becomes crystalline and less soluble by long immersion in water, and by exposure to a low temperature.

Black or magnetic oxide of iron, Ferroso-ferric oxide, $FeO.Fe_2O_3$, an important ore of iron, is a compound of the two oxides. It crystallises in regular octohedrons. In this compound, the sesquioxide of iron may be replaced by alumina and by oxide of chromium, and the protoxide of iron by oxide of zinc, magnesia, and protoxide of manganese, without change of form. It was produced artificially, by Liebig and Wöhler, by mixing the dry protochloride of iron with an excess of carbonate of soda, calcining the mixture in a crucible, and treating the mass with water. The double oxide then remains as a black powder, which may be washed and dried without further oxidation. The same chemists, by dissolving the black oxide in hydrochloric acid, and precipitating by ammonia, obtained a hydrate of the double oxide. It was attracted by the magnet, even when in the state of a flocculent precipitate suspended in water. When ignited and anhydrous, this double oxide is much more magnetic than iron itself.

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* Péan de St. Gilles, *Ann. Ch. Phys.* [3], xlvi. 47.

Scale-oxide, $6FeO . Fe_2O_3$. — When iron is heated to redness in contact with air, two layers of scale-oxide are formed, which may be easily separated. The inner layer, which has the composition just given, is blackish grey, porous, brittle, and attracted by the magnet. The outer layer contains a larger proportion of ferric oxide; it is of a reddish iron-black colour, dense, brittle, yields a black powder, and is more strongly attracted by the magnet than the inner layer. The proportion of ferric oxide in the outer layer is between 32 and 37 per cent., and on the very surface as much as 52·8 per cent. (Mosander). The specific gravity of the scale-oxide is 5·48 (Boullay).

Sesquisulphide of iron, or Ferric sulphide, Fe_2S_3, corresponding with the sesquioxide, may be prepared by pouring a solution of a sesquisalt of iron, drop by drop, into a solution of an alkaline sulphide, the latter being preserved in excess. At a low red heat, it loses 2-9ths of its sulphur, and becomes magnetic pyrites. The common yellow iron pyrites is the *bisulphide of iron.* It crystallises in cubes or other forms of the regular system; its density is 4·981. It may be formed artificially by mixing the protosulphide with half its weight of sulphur, and distilling in a retort at a temperature short of redness. The metallic sulphide combines with a quantity of sulphur equal to that which it already possesses, and forms a bulky powder of a deep yellow colour and metallic lustre, upon which sulphuric and hydrochloric acids have no action. This sulphide appears to be of a stable nature, but the lower sulphides of iron oxidate, when moistened, with great avidity. Stromeyer found the native magnetic sulphide of iron to consist of 100 parts of iron combined with 68 of sulphur; and the sulphide left on distilling iron with sulphur at a high temperature, to be of the same composition. It may be viewed as $5FeS.Fe_2S_3$ (Berzelius). It is said to be this compound which is almost always formed when sulphide of iron is prepared in the usual manner.

Sesquichloride of iron, Ferric chloride, Fe_2Cl_3, is formed when iron is burned in an excess of chlorine. It is volatile at a red heat. Its solution, which is used in medicine, is obtained by dissolving the hydrated sesquioxide of iron in dilute hydrochloric acid. When greatly concentrated, the solution of sesquichloride of iron yields, sometimes orange-yellow crystalline needles, radiating from a centre, which are $Fe_2Cl_3 + 12HO$, at other times, large dark yellowish-red crystals, $Fe_2Cl_3 + 5HO$. Mixed with sal-ammoniac, and evaporated in vacuo, it affords beautiful ruby-red octohedral crystals, consisting of 2 eq. of chloride of ammonium, and 1 eq. sesquichloride of iron, with 2 eq. of water, $Fe_2Cl_3.2NH_4Cl + 2HO$. Of this water, the double salt loses 1 eq. at 150°, and the other when dried above 300° (Graham). There is a similar double salt, containing chloride of potassium, but not so easily formed. Sesquichloride of iron is soluble both in alcohol and ether. A strong aqueous solution was found by Mr. R. Phillips to dissolve not less than 4 eq. of freshly precipitated ferric hydrate, becoming deep red and opaque.

Sesqui-iodide of iron is formed in similar circumstances to the preceding sesquichloride.

Sesquicyanide of iron, Ferric cyanide, Fe_2Cy_3, is unknown in the pure state. A solution of it, which is decomposed by evaporation, is obtained by precipitating the potash of the red prussiate by fluoride of silicon. It forms a numerous class of double cyanides. A compound of the two cyanides of iron, like the compound oxide, is obtained as a green powder, when a solution of the yellow prussiate of potash, charged with excess of chlorine, is heated or exposed to air. The precipitate should be boiled with eight or ten times its weight of concentrated hydrochloric acid, and well washed. Its formula is, $FeCy.\ Fe_2Cy_3 + 4HO$.*

Hydroferricyanic acid; $H_3Fe_2Cy_6$, *or* $H_3.(Cy_3Fc)_2$, *or* $3HCy.Fe_2Cy_3$, is obtained by decomposing ferricyanide of lead with sulphuric or hydrosulphuric acid. The decanted yellow solution yields, by careful evaporation, brownish needles, which redden litmus strongly, and have a rough sour taste. This solution gives a deep blue precipitate (Turnbull's blue), with ferrous salts. This acid, united with salifiable bases, forms the *ferricyanides* $M_3Fe_2Cy_6$. The potassium salt is described in Vol. I. p. 530.

Prussian blue, $Fe_4 \cdot 3(Cy_3Fe)$, *or* $3FeCy.\ 2Fe_2Cy_3$.—This remarkable substance is precipitated whenever the yellow prussiate of potash is added to a sesquisalt of iron. Thus with the sesquichloride:

$$3K_2FeCy_3 + 2Fe_2Cl_3 = Fe_4.3(Cy_3Fe) + 6KCl_3.$$

Care must be taken to avoid an excess of the yellow prussiate, as the precipitate is apt to carry down a portion of that salt. The precipitate also contains water which cannot be separated from it without decomposition. On the large scale, prussian blue is sometimes prepared by precipitating green vitriol with yellow prussiate of potash, and subjecting the white precipitate, KFe_2Cy_3, to the action of oxidising agents, such as chlorine or nitric acid. This process, however, is likely to yield ferricyanide of iron and potassium, KFe_4Cy_6 (p. 40.), rather than prussian blue, properly so called.

Prussian blue, dried at the temperature of the air, is a light porous body, of a rich velvety blue colour; dried at a higher temperature it is more compact, and exhibits in mass a coppery lustre. It is tasteless, and not poisonous. Alkalies decompose it, precipitating sesquioxide of iron and reproducing an alkaline ferrocyanide. This renders prussian blue of little value in dyeing, as it is injured by washing with soap. Red oxide of mercury boiled with prussian blue, affords the soluble cyanide of mercury, with an insoluble mixture of oxide and cyanide of iron. Prussian blue is destroyed by fuming nitric acid, but combines with oil of vitriol, forming a white pasty mass, which is decomposed by water.

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* Pelouze, Ann. Ch. Phys. [2], lxix. 40.

The combination of prussian blue and sesquioxide of iron, called *basic prussian blue,* was noticed at page 40.

Although there is no *carbonate of the sesquioxide of iron,* the hydrated sesquioxide is dissolved by alkaline bicarbonates, under certain conditions which are not well understood, and a red solution is formed.

Ferric sulphates.—The neutral sulphate, $Fe_2O_3.\ 3SO_3$, is formed by adding to a solution of the protosulphate, half as much sulphuric acid as it already contains, and oxidising by nitric acid. It gives a syrupy liquid, without crystallising. This salt is found native in Chili, forming a bed of considerable thickness. It is generally massive, but forms also six-sided prisms, with right summits, which are colourless, and contain 9HO (Rose). Ferric sulphate is soluble in alcohol. It may be rendered anhydrous by a low red heat; but after ignition, it dissolves in water with extreme slowness, like calcined alum.

When hydrated ferric oxide is digested in the neutral sulphate, a red solution is formed, which, according to Maus, is the compound $Fe_2O_3.\ 2SO_3$. The rusty precipitate which is formed in a solution of the protosulphate from absorption of oxygen, is another subsulphate, of which the empirical formula is $2Fe_2O_3.\ SO_3$. The decomposition may be represented by the following equation:—

$$10(FeO.SO_3) + 5O = 2Fe_2O_3.SO_3 + 3(Fe_2O_3.3SO_3).$$

The neutral ferric sulphate remains in solution.

A *potassio-ferric sulphate,* or *iron alum,* is formed by evaporating a solution of the mixed salts to their point of crystallisation. It is colourless and exactly analogous in composition to ordinary alum (I. 606.). Its formula is $KO \cdot SO_3 + Fe_2O_3 . 3SO_3 + 24HO$.

Another double sulphate is formed, which crystallises in large six-sided tables, and of which the formula is $2(KO \cdot SO^3) + Fe_2O_3 \cdot 2SO_3 + 6HO$ (Maus), when potash is added gradually to a concentrated solution of ferric sulphate, till the precipitate formed ceases to redissolve, and the solution is evaporated in vacuo.

Berzelius designates as *ferroso-ferric sulphate* a combination containing $FeO \cdot SO_3 + Fe_2O_3 \cdot 3SO_3$. It is the salt produced when a solution of the neutral protosulphate of iron is exposed to the air, till no more ochre is precipitated. The solution, which is yellowish red, does not crystallise, but gives the black oxide of iron when precipitated by an alkali. A salt of the same constituents, but in different proportions, forms large stalactites, composed of little transparent crystals, in the copper mine of Fahlun. This last is represented by $3FeO \cdot 2SO_3 + 3(Fe_2O_3 \cdot 2SO_3) + 36HO$ (Berzelius).

Ferric nitrate. — By dissolving iron in nitric acid, without heat, as in Schœnbein's experiments (page 35), a salt is obtained in large, transparent, colourless crystals. From more than one analysis, Pelouze found the constituents of this salt to be in the proportion of $2Fe_2O_3.3NO_5 + 1\frac{1}{2}HO$. Its solution is decomposed by heat, with deposition of ferric oxide. Ordway*, by digesting metallic iron in nitric acid of sp. gr. 1·20, obtained, first a greenish solution, then a red, and ultimately a rusty brown precipitate; and on adding an equal volume of nitric acid of sp. gr. 1·43 as soon as the last precipitate began to form, and cooling the liquid below 60°,—or by evaporating the greenish solution, adding a large excess of nitric acid and cooling,—colourless, oblique, rhombic prisms, were formed containing $Fe_2O_3 \cdot 3NO_5 + 18HO$; they were deliquescent, sparingly soluble in nitric acid, melted at about 116° to a red liquid, and gave off their acid partly at 212°, completely at a red heat. Two ounces of these crystals pounded and mixed with an equal weight of pulverised bicarbonate of ammonia, produced a fall of temperature from +58° to −5°. By adding this compound to recently precipitated ferric hydrate, Ordway obtained basic salts containing from 1 to 8 eq. oxide to 1 eq. acid. The solutions of these salts were of a deep red colour; were not decomposed by boiling or dilution; but when they contained a large excess of oxide, were decomposed by the addition of chloride of sodium and other salts. Hausmann*, by evaporating the solution of iron in nitric acid to a syrup, adding half the volume of strong nitric acid, and leaving the solution to crystallise, obtained colourless prisms containing $Fe_2O_3 . 3 NO_5 + 12 HO$. By mixing a very concentrated solution of this neutral salt with water till the colour became reddish yellow, then boiling, and adding nitric acid after cooling, an ochre-coloured precipitate was formed, containing $8 Fe_2O_3 \cdot 2 NO_5 + 3 HO$. By adding a very large quantity of water to a highly concentrated and slightly acid solution of the nitrate, an ochre-coloured precipitate was sometimes formed, containing $36 Fe_2O_3.NO_5 + 48HO$. By treating iron in excess with nitric acid, a precipitate was obtained having the composition $8Fe_2O_3.NO^5 + 12HO$.

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* Sill. Am. J. [2], ix. 30.

Ferric oxalate is very soluble and does not crystallise. It forms a double salt with oxalate of potash, of a rich green colour, of which the formula is $3(KO.C_2O_3) + Fe_2O_3.3C_2O_3 + 6HO$. The crystals effloresce in dry air. In this double salt, the ferric oxide may be replaced by alumina or oxide of chromium. This salt is formed by dissolving hydrated ferric oxide to saturation in bioxalate of potash (salt of sorrel), and crystallises readily from a concentrated solution. The circumstance of its being the salt of sesquioxide of iron most easily obtained and preserved in a dry state, should recommend it as a pharmaceutical preparation.

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* Ann. Ch. Pharm. lxxxix. 100.

The *benzoate and succinate of ferric oxide* are insoluble precipitates. Hence the benzoate and succinate of ammonia are employed to separate iron from manganese. As both these precipitates are dissolved by acids, the iron solution should be made as neutral as possible. The formula of the succinate is, $Fe_2O_3.\bar{S}$.

Ferric acid, FeO_3.—This compound, which is analogous to manganic acid, is obtained in the form of a potash-salt by exposing metallic iron or ferric oxide to the action of powerful oxidising agents. 1. A mixture of 1 part iron-filings and 2 parts nitre is projected into a capacious crucible kept at a dull red heat, and the crucible removed from the fire as soon as the mixture begins to deflagrate and form a white cloud; if the heat is too strong, the compound decomposes as fast as it is formed. The soft, somewhat friable mass of ferrate of potash thus obtained, may be taken out with an iron spoon, and preserved in well stoppered bottles; or the ferrate of potash may be obtained in solution by treating the fused mass with ice-cold water, leaving the liquid to stand to allow the undissolved ferric oxide to settle down, and then decanting; the solution must not be filtered, as it is immediately decomposed by contact with organic matter. 2. Ferrate of potash is also formed by igniting ferric oxide with hydrate of potash in an open crucible, or with a mixture of hydrate of potash and nitre. 3. Chlorine gas is passed through a very strong solution of caustic potash containing hydrated ferric oxide in suspension, fragments of solid potash being continually added in order to maintain a large excess of alkali in the liquid. The ferrate of potash, being almost insoluble in the strong alkaline liquid, is deposited in the form of a black powder, which may be freed from the greater part of the mother-liquor by drying it on a plate of porous earthenware.

Ferrate of potash is a very unstable compound, and has not been obtained in the crystalline form. Its solution is of a deep red colour, like that of permanganate of potash. The acid has not been obtained in the free state; it appears indeed to be scarcely capable of existing in that state, decomposing, as soon as liberated, into oxygen and ferric oxide. *Ferrate of baryta* is formed by adding a solution of ferrate of potash to a dilute solution of a baryta-salt; it then falls down as a deep carmine-coloured precipitate, which may be washed and dried without changing colour. It gives off oxygen when heated, and is readily decomposed by acids.

Nitroprussic acid; $Fe_2Cy_5(NO_2).H_2$. This acid and its salts were discovered by Dr. Lyon Playfair.* It is formed by the action of nitric acid (or rather of nitric oxide) on hydroferrocyanic acid or a ferrocyanide. The hydroferrocyanic acid is first converted into hydroferricyanic acid:

$$4H_2FeCy_3 + NO_2 = 2H_3Fe_2Cy_6 + 2HO + N;$$

and afterwards, by the further action of the nitric oxide, into nitroprussic acid:

$$H_3Fe_2Cy_6 + NO_2 = Fe_2Cy_5(NO_2).H^2 + HCy.$$

Cyanogen is also evolved and oxamide deposited; but these products are due to a secondary action.

To prepare the potassium or sodium salt, ferrocyanide of potassium (2 eq.) is digested in the cold with ordinary nitric acid (5 eq.) diluted with an equal bulk of water, till it is completely dissolved; the solution boiled till it forms with ferrous salts no longer a dark blue, but a green or slate-coloured precipitate, and then left to crystallise, whereupon it deposits a large quantity of nitre, together with oxamide. The strongly coloured mother-liquor is neutralised with carbonate of potash or soda; boiled; filtered to separate a green or brown precipitate; and again left to crystallise. Nitrate of potash or soda then crystallises out first; and afterwards, by further evaporation, the nitroprussiate. The *sodium-salt* crystallises most readily, forming large ruby-coloured prisms, which dissolve in 2½ parts of water at 60°, and in a smaller quantity of hot water. From the solution of this salt, the silver-salt may be obtained by double decomposition; and this, when decomposed by hydrochloric acid, yields nitroprussic acid. This acid crystallises in dark red, very deliquescent, oblique prisms, which dissolve very readily in water, alcohol, and ether. The aqueous solution is very prone to decomposition.

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* Phil. Trans. 1849, ii. 477.

The general formula of the *nitroprussiates* or *nitroprussides* is $Fe_2Cy_5(NO_2).M_2$*: the radical (which might be called *nitro-ferrocyanogen*) may be regarded as 2 eq. of ferrocyanogen, or 1 eq. of ferricyanogen, Fe_2Cy_6, in which 1 eq. of cyanogen is replaced by nitric oxide, NO_2. Most of them are strongly coloured; the ammonium, potassium, sodium, barium, strontium, calcium, and lead salts, dissolve readily in water, forming deep red solutions from which the salts are not precipitated by alcohol. The other nitroprussiates are insoluble, or sparingly soluble. A solution of a nitroprussiate forms, with the solution of an alkaline sulphide, a splendid blue or purple colour, which affords an extremely delicate test of the presence, either of a nitroprussiate, or of an alkaline sulphide.

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* This formula was proposed by Gerhardt. Playfair originally gave the formula $Fe_3Cy_{12}(NO)_3.M_5$; and subsequently (*Phil. Mag.* [3.] xxxvi. 360) suggested the simpler formula, $Fe_2Cy_5(NO).M_2$. Gerhardt's formula, however, agrees quite as well with the analyses of the best defined nitroprussiates as either of these, and is more in accordance with certain reactions; viz., that nitroprussiate of sodium, exposed to sunshine, actually gives off nitric oxide; and that when a solution of the barium-salt is treated with red oxide of mercury, part of the nitrogen is converted into nitric acid.

QUANTITATIVE ESTIMATION OF IRON.

Iron is always estimated in the form of sesquioxide. If the solution contains protoxide, either alone or mixed with sesquioxide, it is first boiled with a sufficient quantity of nitric acid to convert the whole of the protoxide into sesquioxide, and then treated with ammonia in excess to precipitate the latter. The precipitate is collected on a filter, washed, dried, and ignited at a moderate red heat; too high a temperature expels a portion of the oxygen. Every 10 parts of pure sesquioxide correspond to 7 parts of metallic iron. In some cases, however, it is necessary to use potash as the precipitant. In that case, the precipitated ferric oxide is very apt to carry down with it a portion of the potash, which is exceedingly difficult to remove by washing. It is best therefore, after having washed it two or three times with hot water, to re-dissolve it in acid and precipitate by ammonia. In other cases, as when the solution contains organic matter, the iron must be precipitated by sulphide of ammonium, because such substances prevent the precipitation of the oxide. The precipitated sulphide, after being washed, is then dissolved in nitric acid, and the iron precipitated by ammonia as before.

Volumetric method.—The quantity of iron in a solution may also be estimated by reducing it all to the state of protoxide, either by sulphurous acid or by metallic zinc (in the former case the excess of sulphurous acid must be expelled by boiling), and then adding, from a graduated burette, a quantity of solution of permanganate of potash, sufficient to convert all the protoxide of iron into sesquioxide:

$$KO \cdot Mn_2O_7 + 10FeO = 2MnO + KO + 5Fe_2O_3.$$

The liquid must contain an excess of acid, to hold the oxide of manganese in solution. The first portions of permanganate added produce no visible effect; but as soon as all the protoxide of iron is converted into sesquioxide, the addition of another drop of the permanganate imparts a rose tint to the liquid. The value of the solution of the permanganate must be previously ascertained by dissolving 1 gramme of iron (harpsichord wire) in hydrochloric acid, and determining the number of divisions of the burette occupied by the quantity of the solution required to convert that quantity of iron into sesquioxide. (Margueritte, *Ann. Ch. Phys.* [3], 18, 244.)

The preceding method may also be applied to determine the quantities of protoxide and sesquioxide of iron in a solution when they occur together,—viz., by first treating a portion of the solution, as it is, in the manner just described; then taking another equal portion, reducing all the iron in it to protoxide by sulphurous acid, and applying the same method to the solution thus reduced. The first determination gives the quantity of iron in the state of protoxide; the second, the total quantity present: the difference is therefore the quantity in the form of sesquioxide.

Separation of iron from the metals previously described.—From the *alkalies* and *alkaline earths*, iron is separated by ammonia, after having been brought to the state of sesquioxide. In the case of the alkaline earths, care must be taken to add but a slight excess of ammonia, to filter quickly, and exclude the air as completely as possible during the filtration; otherwise the free ammonia will absorb carbonic acid from the air, and then throw down the earths in the form of carbonates, together with the ferric oxide. Should such precipitation occur,—which may generally be known by the colour of the oxide,—the precipitate must be re-dissolved and the treatment with ammonia repeated. If the solution contains fixed organic substances, such as sugar, tartaric acid, &c., the iron must be precipitated by sulphide of ammonium, and the precipitate treated in the manner already described (p. 56.)

From *alumina* and *glucina*, iron is separated by potash, which precipitates the iron, but holds the alumina or glucina in solution. The precipitate, which always contains potash, must then be re-dissolved in acid, and the iron re-precipitated by ammonia.

The separation of iron from *zirconia*, *yttria*, and *thorina*, is effected by adding a sufficient quantity of tartaric acid to prevent the earths from being precipitated when the solution is rendered alkaline, and throwing down the iron by sulphide of ammonium.

From *magnesia* and from *manganous oxide*, iron is most effectually separated by succinate or benzoate of ammonia. The solution, after all the iron has been brought to the state of sesquioxide, is mixed with a sufficient quantity of sal-ammoniac to hold the magnesia or manganous oxide in solution, and very carefully neutralised with ammonia; it is then treated with benzoate or succinate of ammonia, which throws down the iron as ferric benzoate or succinate, leaving the magnesia or manganous oxide in solution. The precipitate is washed and dried, and ignited in an open platinum crucible, so that the air may have sufficient access to it to prevent any reduction of the iron by the carbon of the organic acid. Should such reduction take place, the iron must be re-oxidized by nitric acid. The success of this mode of separation depends entirely on the care with which the acid in the solution is neutralised with ammonia before adding the benzoate or succinate. If too much ammonia has been added, manganese or magnesia goes down with the iron; if too little, a portion of iron remains in solution. The addition of ammonia should be continued till a small quantity of ferric oxide is precipitated, and does not re-dissolve on agitation. The supernatant liquid has then a deep brown colour, the greater part of the iron being still in the solution.

The separation of ferric oxide from manganous oxide may also be effected by agitating the solution with excess of carbonate of lime or baryta, which precipitates the iron but not the manganese. According to J. Schiel*, manganese may be separated from iron by mixing the solution with acetate of soda and passing chlorine through it; bioxide of manganese is then alone precipitated. The methods of separation given at page 7. serve very well for preparing a pure salt of manganese from a solution containing that metal together with iron, but are not adapted for quantitative analysis.

Aridium? This name was given by Ullgren to a metal which he believed to exist in the chrome-iron ores of Röros in Sweden, and in the iron ores of Oernstolso. Its characters very much resemble those of iron. It forms two oxides analogous to those of iron, and presenting, both with liquid reagents and with the blowpipe, characters which might be exhibited by oxides of iron containing a little chromium (vid. *Chem. Gaz.* 1854, 289); Bahr (*Ann. Ch. Pharm.* lxxxvii. 264), endeavoured to prepare the supposed new metal by Ullgren's process, and came to the conclusion that it was merely iron containing a little phosphorus, and perhaps also chromium.

SECTION III.

COBALT.

Eq. 29·52, *or* 369; Co.

Cobalt occurs in the mineral kingdom chiefly in combination with arsenic, as arsenical cobalt, CoAs; or with sulphur and arsenic, as grey cobalt ore, $CoAs.CoS_2$, but contaminated with iron, nickel, and other metals. Its name is that of the Kobolds or evil spirits of mines, and was applied to it by the

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[*] Sill. Am. J. [2], xv. 275.

superstitious miners of the middle ages, who were often deceived by the favourable appearance of its ores. These remained without value, till the middle of the sixteenth century, when they were first applied to colour glass blue. They are now consumed in great quantity for the blue colours of porcelain and stoneware. Cobalt is likewise found in almost all meteoric stones.

To obtain metallic cobalt, the native arsenide is repeatedly roasted, by which the greater part of the arsenic is converted into arsenious acid, and carried off in vapour, while the impure oxide of cobalt, known as *zaffre,* remains. This is dissolved in hydrochloric acid, and the remaining arsenic precipitated as sulphide, by passing a stream of sulphuretted hydrogen through the solution. To get rid of the iron present, the last solution, after filtration, is boiled with a little nitric acid, to peroxidise that metal; and carbonate of potash is added in excess, which throws down carbonate of cobalt and sesquioxide of iron. The precipitate is treated with oxalic acid, which forms an insoluble oxalate of cobalt and soluble ferric oxalate. The oxalate of cobalt is dried and decomposed by ignition in a covered crucible, when the oxide is reduced by the carbon of the acid, which goes off as carbonic acid, while the metallic cobalt remains as a black powder. To separate cobalt from nickel, with which it is almost always associated, the mixed oxalates of cobalt and nickel, obtained by the preceding process, are dissolved in ammonia, after which the liquid is diluted and exposed to the air in a shallow basin for several days. The ammonia evaporates, and the salt of nickel precipitates as a green powder, while the salt of cobalt remains in solution. The liquid is then decanted, and if no additional precipitate subsides from it in twenty-four hours, it is free from nickel, and may be evaporated to dryness. The precipitate of nickel contains a little cobalt.*

Cobalt is a brittle metal, of a reddish grey colour, some-

* For other methods of separating nickel and cobalt, see *Nickel.*

what more fusible than iron, and of the density 8·5131 (Berzelius). Rammelsberg, in five experiments with cobalt reduced by hydrogen, found the specific gravity to vary from 8·132 to 9·495; the mean is 8·957. Pure cobalt is magnetic, but a minute quantity of arsenic causes it to lose that property.

Cobalt is less oxidable in the air or by acids than iron, dissolving slowly in diluted hydrochloric or sulphuric acid, when heated, with evolution of hydrogen; but it is readily oxidised by nitric acid. This metal forms a protoxide and sesquioxide, CoO and Co_2O_3, corresponding with the oxides of iron, and three intermediate oxides, viz., $Co_3O_4 = CoO.Co_2O_3$; $Co_6O_7 = 4CoO.Co_2O_3$; and $Co_8O_9 = 6CoO.Co_2O_3$. According to Fremy, the first of these, viz., Co_3O_4 is a salifiable base combining directly with acetic acid, and existing in several ammonio-salts of cobalt. Fremy has also obtained compound salts of this nature containing a bioxide of cobalt CoO_2

Protoxide of cobalt, Cobaltous oxide, CoO, 37·52 *or* 469.—Prepared by the ignition of the carbonate. This oxide is a powder of an ash-grey colour. It colours glass blue, even when in minute quantity, no other colouring matter having so much intensity. *Smalt blue* is a pounded potash-glass containing cobalt. All compounds of cobalt, when heated with *borax* or *phosphorus-salt,* either in the inner or in the outer blowpipe-flame, impart a splendid blue colour to the bead. This coloration affords an extremely delicate test for cobalt.

The salts of protoxide of cobalt have a reddish colour in solution. *Potash* or *soda* added to these solutions forms a blue precipitate of the hydrated oxide, insoluble in excess of the reagent. *Ammonia* also forms a blue precipitate, which dissolves in excess of ammonia, yielding a red-brown solution. If the cobalt solution contains a large quantity of free acid or of an ammoniacal salt, no precipitate is formed by ammonia. *Alkaline carbonates* precipitate a pink carbonate of cobalt, soluble in *carbonate of ammonia*. *Hydrosulphuric acid* does not precipitate a solution of cobalt containing either of the stronger acids; but in a solution of acetate of cobalt, or of any cobalt-salt mixed with acetate of ammonia, it forms a black precipitate of protosulphide of cobalt. *Alkaline sulphides* throw down the same precipitate from all solutions of protoxide of cobalt.

Oxide of cobalt appears to combine with alkalies and earths as well as with acids. It dissolves in fused potash, and imparts a blue colour to the compound. Magnesia mixed with a drop of nitrate of cobalt, and then dried and ignited, assumes a feeble but characteristic rose tint. A compound of oxide of cobalt with alumina is obtained by mixing the solution of a salt of cobalt, which must be perfectly free from iron or nickel, with a solution of equally pure alum, precipitating the liquor by an alkaline carbonate, washing the precipitate with care, then drying and igniting it strongly. It forms a beautiful blue pigment, known as cobalt-blue, which may be compared in purity of tint with ultramarine. A compound of oxide of cobalt with oxide of zinc of a fine green colour may be prepared in a similar manner. These coloured compounds often afford useful confirmatory tests of the presence of zinc, alumina, or magnesia. The substance to be examined is placed on platinum foil, moistened with nitrate of cobalt, then dried, and strongly heated in the blowpipe-flame.

Chloride of cobalt, $CoCl$, is obtained by dissolving zaffre or the oxide in hydrochloric acid. Its solution is pink-red, and affords hydrated crystals of the same colour; but when highly concentrated, assumes an intense blue colour, and then affords blue crystals of chloride of cobalt, which are anhydrous (Proust). The red solution is used as a sympathetic ink; characters written with it on paper are colourless and invisible, or nearly so, but when the paper is warmed by holding it near a fire or against a stove, the writing becomes visible and appears of a beautiful blue. After a while, as the salt absorbs moisture, the colour again disappears, but may be reproduced by the action of heat. If the paper be exposed to too high a temperature, the writing becomes black, and does not afterwards disappear. The addition of a salt of nickel to the sympathetic ink gives a green instead of blue.

The neutral *carbonate of cobalt* is unknown, oxide of cobalt, like magnesia, being thrown down from its solutions by alkaline carbonates, as a carbonate with excess of oxide. The subcarbonate of cobalt is a pale red powder, which contains, according to Setterberger, 2 eq. of carbonic acid, 5 eq. of oxide of cobalt, and 4 eq. of water.

Besides the *sulphate of cobalt* corresponding with green vitriol, another salt was crystallised by Mitscherlich between 68° and 86°, containing 6 eq. of water, $CoO.SO_3+6HO$, isomorphous with a corresponding sulphate of magnesia. Sulphate of cobalt forms the usual double salts with the sulphates of potash and ammonia, containing 6HO.

Nitrate of cobalt, $CoO.NO_5$—is obtained by dissolving the metal, the protoxide, or the carbonate in dilute nitric acid. Its solution is carmine-coloured, and on evaporation yields red crystals containing 6 eq. of water; they deliquesce in the air, fuse below 100°, and at a higher temperature give off water and melt into a violet-red liquid, which afterwards becomes green and thick, and is ultimately converted, with violent intumescence and evolution of nitrous fumes, into black sesquioxide of cobalt. Characters written on paper with a solution of this salt assume a peach-blossom colour when heated.

A *sexbasic nitrate*, $6CoO.NO_5+5Aq.$, is obtained on adding excess of ammonia to a well boiled solution of the neutral nitrate, carefully protected from the air. It then falls down as a blue precipitate, but on the slightest access of air quickly assumes a grass-green colour and partly redissolves in the liquid.

Cobalt-yellow, $CoO.KO.N_2O_8$.—This compound is formed by adding a solution of nitrite of potash (obtained by passing the nitrous fumes evolved from a heated mixture of nitric acid and starch into caustic potash) to an acid solution of nitrate of cobalt; nitric oxide and nitrate of potash are then formed, and the cobalt-compound separates in the form of a beautiful yellow crystalline powder:

$$CoO.NO_5 + 2NO_5 + 4(KO.NO_3) = 3(KO.NO_5) + 2NO_2 + N_2O_8.CoO.KO.$$

It is likewise obtained by adding potash, not in excess, to solution of nitrate of cobalt, so as to precipitate a blue basic salt, treating this with a slight excess of nitrite of potash, and adding nitric acid in a thin stream, by means of a pipette. Also by treating nitrate of cobalt with a slight excess of potash, so as to throw down the rose-coloured hydrated oxide, and passing nitric oxide gas into the mixture. This last reaction is so rapid that it may be exhibited as a lecture-experiment. The compound crystallises in microscopic four-sided prisms with pyramidal summits. It is insoluble in cold water, also in alcohol and ether, but when boiled with water gradually dissolves with evolution of acid vapours; the solution yields on evaporation a lemon-yellow salt of different composition. Nitric acid and hydrochloric acid do not act upon it in the cold, but decompose it at a boiling heat, with evolution of nitrous fumes. Hydrosulphuric acid decomposes it very slowly, sulphide of ammonium immediately, forming black sulphide of cobalt. When heated, it assumes an orange-yellow colour, gives off water and afterwards fumes of nitric and hyponitric acids, and leaves sesquioxide of cobalt mixed with nitrite of potash. Its beautiful colour, its permanence, and the facility with which it mixes with other colours, render it well adapted for artistic purposes.*

According to A. Stromeyer†, this salt is a nitrite of cobaltic oxide and potash, $Co_2O_3.2NO_3+3(KO.NO_3)$, and its formation may be represented by the equation,

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* St. Evre, Ann. Ch. Phys. [3], xxxviii. 177.

† Ann. Ch. Pharm. xcvi. 218.

$$2(CoO.SO_3)+5(KO.NO_3)+O=[Co_2O_3.2NO_3+3(KO.NO_3)] \\ +2(KO.SO_3).$$

When a solution of lead is mixed with nitrite of potash and acetic acid, the liquid assumes a yellow colour, but no precipitation takes place; but on adding a cobalt-salt, a yellowish green precipitate (or brownish black and crystalline from dilute solutions) is formed, whose composition is that of the yellow cobalt-compound with half the potash replaced by oxide of lead (Stromeyer).

Phosphate of cobalt, $2CoO.HO.PO_5$, is an insoluble precipitate of a deep violet colour. When 2 parts of this phosphate or 1 part of the arseniate of cobalt are carefully mixed with 16 parts of alumina and strongly ignited for a considerable time, a beautiful blue pigment is obtained, resembling ultramarine; it was discovered by Thénard.

Arseniate of cobalt, $3CoO.AsO_5 + 8HO$, exists as a crystalline mineral called *cobalt-bloom.*

Sesquioxide of cobalt, Cobaltic oxide, Co_2O_3, is formed when chlorine is transmitted through water in which the hydrated protoxide is suspended, or when a salt of the protoxide is precipitated by a solution of chloride of lime. In the former case, water is decomposed by the chlorine, and hydrochloric acid produced, while the oxygen of the water peroxidises the cobalt;

$$2CoO + HO + Cl = Co_2O_3 + HCl.$$

The sesquioxide of cobalt is precipitated as a black hydrate, containing 2HO. This hydrate, when cautiously heated to 600° or 700°, yields the black anhydrous oxide. When sesquioxide of cobalt is digested in hydrochloric acid, chlorine is evolved, and the protochloride formed. Exposed to a low red heat, the sesquioxide loses oxygen, and the compound oxide, $CoO.Co_2O_3$, is produced. (Hess.) When protoxide of cobalt is calcined with a borax glass, at a moderate heat, it absorbs oxygen, and a black mass is obtained, which mixed with manganic oxide, serves as a black colour in enamel painting.

Sesquioxide of cobalt acts as a weak base. Phosphoric, sulphuric, nitric, and hydrochloric acids dissolve its hydrate in the cold, without decomposition at first, but the resulting salts are afterwards reduced to salts of the protoxide. A protosalt of cobalt containing a small quantity of a sesquisalt is somewhat deepened in colour. The most permanent of the sesquisalts is the acetate; the hydrated sesquioxide while yet moist dissolves in acetic acid, slowly but completely. The solution, which has an intense brown colour, forms a brown precipitate with alkalies and alkaline carbonates. With ferrocyanide of potassium it forms a dark precipitate, which, if the precipitant is in excess, gives up cyanogen to it, converting it into ferricyanide of potassium and being itself converted into green ferrocyanide of cobalt. Alkaline oxalates colour the solution yellow, forming an oxalate of the oxide Co_3O_4.

According to Fremy, the oxide Co_3O_4 combines also with other acids. The acetate of this oxide is obtained by digesting in dilute acetic acid the hydrated oxide obtained by continued action of oxygen on the blue precipitate thrown down from ordinary cobalt-salts by potash not in excess. Fremy also states that when chlorine is passed into the solution of ordinary acetate of cobalt, a brownish yellow salt is formed containing the base Co_3ClO_3, or Co_3O_4 in which 1 eq. of O is replaced by Cl. This chlorine base exists also in some of the ammonio-compounds of cobalt (pp. 68-72). The oxide Co_3O_4 is obtained in the free state by heating the nitrate or oxalate of cobalt, or the hydrated sesquioxide to redness in contact with the air (Hess, Rammelsberg); but according to Beetz and Winkelblech, the oxide thus obtained is Co_6O_7. When the residue obtained by gently igniting the oxalate in contact with the air is digested in strong boiling hydrochloric acid, the oxide Co_3O_4 remains in hard, brittle, greyish-black microscopic octohedrons having a metallic lustre. The same crystalline compound is obtained by igniting dry protochloride of cobalt, alone or mixed with sal-ammoniac, in dry air or oxygen gas (Schwarzenberg).

A *cobaltic acid*, Co_3O_5, is obtained in combination with potash by strongly igniting the oxide Co_3O_4, or the protoxide, or the carbonate, with pure hydrate of potash. A crystalline salt is then formed which, when dried at 100° C., contains $KO.3Co_3O_5+3HO$, and gives of 1 eq. of water at 130° (Schwarzenberg).

Bioxide of cobalt, CoO_2, has not been obtained in the free state, but exists according to Fremy in the oxycobaltiac salts. (p. 68.)

There exist three *sulphides of cobalt*, a protosulphide, sesquisulphide, and bisulphide.

Sesquicyanide of cobalt has not been obtained in the separate state, but it exists in a class of double cyanides, of which the radical is cobalticyanogen, Cy_6Co_2, analogous to ferricyanogen. The cobalticyanide of potassium, corresponding with the red prussiate of potash, is formed when protoxide of cobalt or its carbonate is dissolved in caustic potash which has been treated with an excess of hydrocyanic acid. It is an anhydrous salt, pale yellow and nearly colourless when pure, and of the same form as the ferricyanide of potassium. Its solution does not affect the salts of iron, but forms a rose-coloured precipitate with those of the protoxide of cobalt.*

A *phosphide of cobalt*, Co_3P, was obtained by Rose, as a grey powder, on passing hydrogen over the subphosphate of cobalt ignited in a porcelain tube. It is also produced by the action of phosphuretted hydrogen on the chloride of cobalt, and may be looked upon as analogous in composition to the former compound, H_3P.

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* For further details on the cobalticyanides, *vide* Gmelin's Handbook (translation), vii. 492—497.

Ammoniacal salts of cobalt.—Cobalt-salts treated with excess of ammonia in a vessel from which the air is excluded, unite with the ammonia, forming compounds to which Fremy gives the name of *ammonio-cobalt salts*. Most of them contain 3 eq. ammonia to 1 eq. of the cobalt-salt; thus the chloride contains $CoCl.3NH_3+HO$: the nitrate $CoO.No_5.3NH_3+2HO$. They are mostly crystallisable and of a rose-colour, soluble without decomposition in ammonia, but decomposed by water with separation of a basic salt. (Fremy.) H. Rose, by treating dry chloride of cobalt with ammoniacal gas, obtained the compound $CoCl.2NH_3$; and similarly an anhydrous sulphate containing $CoO.SO_3.3NH_3$.

When an ammoniacal solution of a cobalt salt is exposed to the air, oxygen is absorbed, the liquid turns brown, and new salts are formed containing a higher oxide of cobalt (Co_2O_3 or CO_2), and therefore designated generally as *peroxidised ammonio-cobalt salts*. Several of these salts containing different bases are often formed at the same time. Fremy* distinguishes four classes of these compounds, viz., salts of *oxycobaltia, luteocobaltia, fuscocobaltia,* and *roseocobaltia.*

The *oxycobaltia-salts* are formed by the action of the air on concentrated solutions of ammonio-cobalt salts. They have generally an olive colour, are sparingly soluble in the ammoniacal liquid, and are decomposed by water, especially when hot, with evolution of pure oxygen, liberation of ammonia, and separation of a green basic salt containing cobaltoso-cobaltic oxide CO_3O_4. They contain 5 eq. of ammonia associated with 2 eq. of a monobasic salt of bi-oxide of cobalt, CoO_2; thus the nitrate is composed of $2(CoO_2.NO_5).5NH_3$. The nitrate and sulphate crystallise in small prisms containing water of crystallisation (Fremy).

The *luteocobaltia-salts* are formed: 1. By the action of the air on dilute solutions of ammonio-cobalt salts; 2. By the action of a small quantity of water on crystallised oxycobaltia-salts; 3. By treating the brown solution, formed by the action of oxygen in excess on ammonio-cobalt salts, with dilute acids; 4. By treating roseocobaltia-salts with excess of ammonia. These salts are of a fine yellow colour, crystallise readily, are tolerably permanent, and resist for some time the action of boiling water. They give no precipitates with alkaline phosphates or carbonates at ordinary temperatures, but are decomposed by boiling potash, with evolution of ammonia and separation of Co_2O_3HO. Dilute acids precipitate them from their aqueous solution in the crystalline state. They contain 1 eq. of a sesquisalt of cobalt, associated with 6 eq. of ammonia; thus, the sulphate $= (Co_2O_3.3SO_3).6NH_3$; the chloride $= Co_2Cl_3.6NH_3$. (Fremy.) This last salt was previously obtained by Rogojski*, who regarded it as the *hydrochlorate of dicobaltinamine* $ClH.N_2H_5co$ [$co = \frac{2}{3}Co$]. He likewise obtained the other salts of the same base by double decomposition.

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* Ann. Ch. Phys., [3], xxxv. 257.; Chem. Gaz. 1853, 201.

Fuscocobaltia-salts are formed when an ammoniacal solution of a protosalt of cobalt is exposed to the air, and by the action of water on the oxycobaltia-salts. They are all uncrystallisable, but may be obtained in the solid state by precipitation with alcohol or excess of ammonia. They are slowly decomposed by boiling with water, but quickly on the addition of an alkali, with evolution of ammonia, and precipitation of hydrated sesquioxide of cobalt. They are of a brown colour, and appear to contain basic salts of sesquioxide of cobalt, united with 4 or 5 eq. of ammonia. The nitrate contains $Co_2O_3.2NO_5.4NH_3.3HO$.

Ammonio-chloride of cobalt, after exposure to the air, yields by evaporation in vacuo, an uncrystallisable residue having the characters of the fuscocobaltia-salts, but containing a chlorine-base; its formula is $Co_2Cl_2O.4NH_3.3HO$. By exposing the solution of the ammonio-chloride to the air for two or three weeks, and then boiling with sal-ammoniac, roseocobaltiacal chloride separates out first, and afterwards a black crystalline compound containing $Co_3ClO_3.NH_3+5HO$.

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* J. pr. Chem. lvi. 491.

The *roseocobaltia-salts* are obtained: 1. By slightly acidulating the solution of an ammonio-cobalt salt, which has been exposed to the air; 2. By boiling the solution of an ammonio-cobalt salt, which has been exposed to the air for two or three days, and contains a fuscocobaltia-salt, with a salt of ammonia; 3. By mixing oxycobaltia-salts with boiling solutions of ammoniacal salts. They have a fine red or rose colour, and some of them crystallise readily. Their reactions are similar to those of the luteocobaltia-salts. The nitrate and the neutral sulphate contain 3 eq. of $Co_2O_3.3NO_5$, or $Co_2O_3.3SO_3$, with 5 eq. ammonia. There is also an acid sulphate containing $(Co_2O_3.5SO_3)5NH_3+5HO$, obtained by adding sulphuric acid in excess to an ammoniacal solution of sulphate of cobalt which has stood for some days in contact with the air. Baryta-water added to the solution of the sulphate, throws down roseocobaltiacal oxide, which is rose-coloured, has a strong alkaline reaction, and decomposes on boiling, giving off ammonia and depositing Co_2O_3. The chloride, $Co_2Cl_3.5NH_3.HO$, is obtained by boiling the ammonio-chloride of cobalt, or the chlorine-compound $Co_2Cl_2O.4NH_3$ (p. 69.), or a salt of oxycobaltia, with chloride of ammonium (Fremy).

Genth[*] and F. Claudet[†] have also described a compound which appears to be the same as Fremy's hydrochlorate of roseocobaltia, although each assigns to it a different formula. When sulphate or chloride of cobalt is mixed with a large quantity of chloride of ammonium and an excess of ammonia, exposed for some time to the air, and then boiled with excess of hydrochloric acid, a crimson powder gradually separates, oxygen is evolved, and the liquid becomes colourless. This compound dissolves in 244 parts of cold water, and in a smaller quantity of boiling water, but is decomposed by continued boiling, unless hydrochloric acid be added; in that case a solution is obtained, from which the compound crystallises on cooling in ruby-coloured regular octohedrons. Genth assigns to this compound the formula $Co_2O_3.3NH_4Cl$, regarding it as the chloride of a conjugated radical $Co_2O_3.3NH_4$. Claudet finds it to contain 3Cl, 2Co, 5N and 16H, and expresses its composition by one of the following formulæ:—

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[*] Ann. Ch. Pharm. lxxx. 275.; Chem. Gaz. 1851, 266.

[†] Phil. Mag. [4], ii. 253.; Chem. Soc. Qu. J. iv. 355.

$$3NH_4Cl + 2NH_2Co; \qquad Cl\left\{\begin{matrix} NH_2Co_2 \\ NH_3NH_4 \\ NHNH_4 \end{matrix}\right\}; \qquad ClN\left\{\begin{matrix} H_2 \\ Co_2 \end{matrix}\right\} + 2ClN\left\{\begin{matrix} H_3 \\ NH_4 \end{matrix}\right\}$$

According to the two latter formulæ, the compound is supposed to contain ammonium in which part of the hydrogen is replaced by NH_4. It might also be regarded as the *hydrochlorate of pentacobaltosamine* $N_5H_{13}Co_2.3HCl$, the base being formed of 5 eq. of ammonia in which 2 eq. of hydrogen are replaced by cobalt. Gregory* assigns to it the formula $Co_2Cl_3 . 5NH_3$, making it identical with Fremy's roseocobaltiacal chloride.

The compound heated in a glass tube gives off ammonia and sal-ammoniac, and leaves CoCl. When the aqueous solution is boiled, ammonia is evolved, and a precipitate formed probably consisting of $Co_3O_4.3HO$, combined with nitride of cobalt. The chlorine compound treated with recently precipitated oxide of silver, yields the oxygen-compound of the same radical; and by double decomposition with various silver-salts, the other salts of the base.

The ammonia in all these compounds is in a peculiar state, not exhibiting its usual basic properties, or being recognisable by the usual reagents or replaceable by other bases. Claus attributes this circumstance to the ammonia being in a *passive* state, which is merely another way of expressing the fact, but affords no explanation. Weltzien supposes the compounds in question to contain compound ammonium-molecules, in which 1 or 2 at. hydrogen are replaced by ammonium itself (an idea first suggested by Mr. Graham), viz., *ammo-cobaltammonium* $\overbrace{NH_2AmCo}$, and *biammo-cobaltammonium* $\overbrace{NHAm_2Co}$ [the symbol Am standing for NH_4]. Thus the *ammonio-cobalt salts,* containing $2NH_3$, may be regarded as neutral salts of ammo-cobaltammonium, and those which contain $3NH_3$ as neutral salts of biammo-cobaltammonium: thus —

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* Ann. Ch. Pharm. lxxxvii. 125.

$$CoCl.2NH_3 = \overbrace{NH_2AmCo}.Cl\text{; and}$$

$$CoBr.3NH_3 = \overbrace{NHAm_2Co}.Br.$$

The *fuscocobaltia-salts* may be regarded as basic salts of the sesquioxide of ammo-cobaltammonium, *e. g.*—

$$Co_2O_3.2NO_5.4NH_3 = (\overbrace{NH_2AmCo})_2O_3.2NO_5.$$

The *luteocobaltia*-salts, as neutral salts of the sesquioxide of biammo-cobaltammonium, *e. g.*—

$$Co_2O_3.3NO_5.6NH_3 = (\overbrace{NHAm_2Co})_2O_3.3NO_5\,;$$

The *roseocobaltia*-salts as neutral sesquisalts containing 1 at. of each of the above-mentioned ammoniums, thus—

$$Co_2Cl_3.5NH_3 = \left.\begin{matrix}\overbrace{NH_2AmCo}\\ \overbrace{NHAm_2Co}\end{matrix}\right\}.Cl_3\,;$$

And the *oxycobaltia-salts* as basic salts of the same two ammonium-molecules, *e. g.*—

$$2CoO_2.2SO_3.5NH_3 = \left.\begin{matrix}\overbrace{NH_2AmCo}\\ \overbrace{NHAm_2Co}\end{matrix}\right\}O_4.2SO_3.$$

ESTIMATION OF COBALT, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Cobalt is generally precipitated from its solutions by caustic potash. The precipitate is bluish, and consists of a basic salt, which, however, when heated, is converted into the hydrated protoxide of a dingy rose colour. It must then be washed in hot water, dried and ignited in an atmosphere of hydrogen, by which it is reduced to the metallic state, after which it is weighed. According to Beetz*, the reduction to the metallic state may be dispensed with, an accurate result being obtained by igniting the precipitated oxide till it no longer varies in weight, its composition being then $4Co.Co_2O_3$ or Co_6O_7; but the reduction by hydrogen is perhaps the surer method.

Cobalt is separated from the *alkalies* and *alkaline earths* by sulphide of ammonium, the black sulphide of cobalt being then dissolved in nitro-hydrochloric acid, and the oxide precipitated by potash as above.

From *magnesia* it may also be separated by sulphide of ammonium, sufficient chloride of ammonium being added to hold the magnesia in solution.

From *alumina* and *glucina* it is separated by potash.

The separation of cobalt from *manganese* is difficult. It is best effected by heating the mixed oxides in hydrochloric acid gas, which converts them into chlorides, and then heating the chlorides in a stream of hydrogen, which reduces the cobalt to the metallic state, but leaves the chloride of manganese undecomposed; the latter is then dissolved out by water. Another mode of separation is to digest the mixed oxides in a solution of pentasulphide of calcium, which dissolves the sulphide of cobalt, but leaves the sulphide of manganese undissolved.†

Cobalt is separated from *iron* in the same manner as manganese (p. 58.), viz. by bringing the iron to the state of sesquioxide, then adding chloride of ammonium, neutralising with ammonia, and precipitating the iron by succinate of ammonia.

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* Pogg. Ann. lxi. 472.

† Cloez, J. Pharm. [3.] vii. 157.

SECTION IV.

NICKEL.

Eq. 29·57 or 369·6.

This metal resembles iron and cobalt more than any others, and is associated with these metals in meteorites, and in most of the terrestrial minerals which contain it. The principal ore of nickel is arsenical nickel, a mineral having the colour of metallic copper, to which the German miners, having attempted in vain to extract copper from it, gave the name *kupfer-nickel,* or false copper. This mineral was found by Cronstedt of Sweden, in 1751, to contain a particular metal, which he called nickel. Nickel imparts a remarkable whiteness to the metallic alloys which contain it, on which account it has come of late to be valued in the arts, being added to brass to form the well-known imitations of silver.

The metal is prepared from the native arsenide, or from an artificial arsenide called *speiss,* which contains about 54 per cent of nickel, and has been observed by Wöhler to occur in octohedrons with a square base, having the composition Ni_3As. Speiss is a metallic substance which collects at the bottom of the crucibles in which smalt or cobalt-blue is prepared. In that operation, a mixture of quartzy sand, potashes, and the roasted ore of cobalt is fused. The previous roasting never being perfect, a part of the metals escapes oxidation; and hence when the mixture described is fused, the cobalt, which is more oxidable than nickel and copper, reacts upon the oxides of these metals, and reduces them, while it is itself oxidated: the nickel and copper concentrate in the speiss, while the smalt contains scarcely any of them. A salt of nickel may be obtained by treating speiss in fine powder with an equal weight of sulphuric acid, diluted with four or five times its bulk of water, and gradually adding an equal weight of nitric acid, which occasions the oxidation of both the nickel and the arsenic. The green solution thus obtained, when cooled and allowed to stand for twenty-four hours, deposits much arsenious acid, from which it may be separated by filtration. A quantity of carbonate of potash, equal to half the weight of the speiss, is then added to the solution, which is concentrated and set aside to crystallise. The double sulphate of nickel and potash, $NiO.SO_3 + KO.SO_3 + 6HO$, forms easily, and may be obtained free from arsenic by a second crystallisation. (Dr. Thomson.) The perfect separation of small quantities of cobalt and copper, which these crystals may still contain, requires additional processes.* With the view of obtaining the metal, the insoluble oxalate of nickel may be precipitated from the preceding salt by oxalate of ammonia, washed, dried, and ignited gently in a covered crucible. The oxalic acid reduces the oxide of nickel, and the metal remains in a spongy state. It is pyrophoric, like manganese and iron prepared in the same manner, if the temperature of reduction has been low. To obtain the metal in a solid mass, it should be fused in a crucible covered with pounded glass. The oxide of nickel is very easily reduced both by carbonic oxide and by hydrogen.

Nickel, when free from cobalt, is silver-white, unalterable in air, and highly ductile. Its density, according to Richter, is 8·279, and after being forged 8·666. Nickel is magnetic nearly to the same extent as iron. Magnets composed of this metal lose their polarity at 630° (Faraday). It is somewhat more fusible than iron. Nickel forms two oxides corresponding with the protoxide and sesquioxide of iron; but the double compound of the two oxides of nickel, corresponding with the black oxide of iron, has not been observed.

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* Berzelius, Traité, tom. i. p. 486.; see also pp. 78—80. of this volume.

Protoxide of nickel, NiO, 37·57, or 469·6, may be obtained by the ignition of the carbonate or nitrate of nickel, or by precipitation from its salts by an alkali, as a dark ash-coloured powder, or as a bulky hydrate of an apple-green colour, NiO HO. Oxide of nickel is very soluble in acids, but not in potash or soda. Ammonia dissolves it, and forms an azure-blue solution, from which oxide of nickel is precipitated by potash, baryta, and strontia, having a considerable tendency to combine with salifiable bases. The solutions of its salts have all a green colour, much more intense than that of the ferrous salts. They are not precipitated by hydrosulphuric acid when a strong acid is present, but afford a black sulphide with alkaline sulphides. Carbonate of nickel is of a pale green-colour and soluble in carbonate of ammonia.

Peroxide or *sesquioxide of nickel,* Ni_2O_3, is obtained as a black powder, by exposing the hydrated protoxide suspended in water to a stream of chlorine gas. It does not combine with acids, aud in other respects resembles sesquioxide of cobalt.

Besides a *protosulphide,* NiS, a *subsulphide of nickel,* Ni_2S, is formed, like that of manganese, by decomposing the ignited sulphate of nickel with hydrogen. A *bisulphide of nickel* also exists in combination as a constituent of the mineral nickel-glance, $NiS_2.NiAs$.

Chloride of nickel NiCl, forms a solution of an emerald-green colour, and yields by evaporation a hydrated salt of the same colour, which becomes yellow when deprived of its water of crystallisation. Chloride of nickel, sublimed at a high temperature without access of air, forms golden scales which dissolve with difficulty.

Sulphate of nickel crystallises from a strong solution in slender green prisms, isomorphous with Epsom salt, of which the composition is $NiO.SO_3 + 7HO$. At a higher temperature, it crystallises with 6 eq. of water $NiO.SO_3+6HO$, like the magnesia and cobalt salts, and in the same form. Mitscherlich made the singular observation, that when the crystals containing 7 eq. of water are exposed, in a close glass vessel, to a day of sunshine, or kept for some time in a temperate place, they change their form, becoming a mass of small crystals, of which the form is the regular octohedron. The original crystals become opaque from this change, but lose none of their combined water. Sulphate of nickel forms the usual double salts with the sulphates of potash and ammonia.

Nickel also forms ammonio-compounds analogous to the ammonio-cobalt salts; *e. g. the ammonio-chloride* = $3NH_3.NiCl = \overbrace{NHAm_2Ni}.Cl$; *ammonio-sulphate* = $3NH_3.NiSO_4 = \overbrace{NHAm_2Ni}.SO_4$, &c.

The useful white *alloy of nickel,* German silver or *packfong,* is formed by fusing together 100 parts of copper, 60 of zinc, and 40 of nickel.

ESTIMATION OF NICKEL, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Nickel is best precipitated from its solutions by caustic potash which throws down an apple-green precipitate of the hydrated protoxide, and if the liquid be heated, leaves not a trace of nickel in the solution. The precipitate must be washed with hot water, dried, ignited, and weighed; it then consists of pure protoxide of nickel, containing 78·57 per cent of the metal.

In separating nickel from other metals, it is often necessary to precipitate it by sulphide of ammonium; this precipitation is attended with difficulties, because the sulphide of nickel is somewhat soluble in the alkaline sulphide. To make the precipitation as complete as possible, Rose directs that the solution be diluted with a considerable quantity of water, and then treated with sulphide of ammonium, as nearly colourless as it can be obtained, avoiding a large excess of the precipitant and likewise an excess of ammonia; the glass is then to be covered up with filtering paper, and left in a warm place. Under these circumstances, the excess of sulphide of ammonium is decomposed by the oxygen and carbonic acid of the air, without risk of the sulphide of nickel being oxidised. As soon as the supernatant liquid has lost its brown colour, the precipitate is collected on a filter and washed, as quickly as possible, with water containing a little sulphide of ammonium. It must then be dissolved in nitro-hydrochloric acid, and the nickel precipitated by potash as above.

The methods of separating nickel from all the preceding metals except cobalt, are the same as those given for cobalt (p. 73.).

The separation of nickel from cobalt itself is difficult. The best method is perhaps that given by H. Rose*, depending on the fact that protoxide of cobalt in solution is converted by chlorine into sesquioxide, whereas with nickel this change does not take place. The metals or their oxides being dissolved in excess of hydrochloric acid, the solution is diluted with a large quantity of water, about a pound of water to a gramme of the metals or their oxides. Chlorine gas is then passed through the solution for several hours, till in fact the space above the liquid becomes permanently filled with the gas; carbonate of baryta is then added in excess, the whole left to stand for 12 or 18 hours, and shaken up from time to time. The precipitate, consisting of sesquioxide of cobalt and carbonate of baryta, is then collected on a filter, and washed with cold water. The filtered liquid, which has a pure green colour, contains all the nickel without a trace of cobalt. The precipitate is boiled with hydrochloric acid to convert the sesquioxide of cobalt into protoxide, and dissolve it together with the baryta; the latter is then precipitated by sulphuric acid, and the cobalt from the filtrate by potash. The nickel is also precipitated by potash after the removal of any baryta that the solution may contain

* Handbuch der Analytischen Chemie (Berlin, 1851), ii. 164.

by sulphuric acid. This method, if properly executed, gives very exact results. The chief precautions to be attended to, are to add a large excess of chlorine, and not to filter too soon, because the precipitation of sesquioxide of cobalt by carbonate of baryta takes a long time.

Liebig has given several methods of separating these two metals, founded on the difference of their reactions with cyanide of potassium. 1. The oxides of the two metals are treated with hydrocyanic acid and then with potash, and the liquid warmed till the whole is dissolved (pure cyanide of potassium, free from cyanate may also be used as the solvent). The reddish-yellow solution is boiled to expel free hydrocyanic acid, whereupon the cobaltocyanide of potassium (K_2CoCy_3), formed in the cold, is converted into cobalticyanide ($K_3Co_2Cy_6$), while the nickel remains in the form of cyanide of nickel and potassium ($KNiCy_2$). Pure and finely-divided red oxide of mercury is then added to the solution while yet warm, whereby the whole of the nickel is precipitated partly as oxide, partly as cyanide, the mercury taking its place in the solution. The precipitate contains all the nickel, together with excess of mercuric oxide; after washing and ignition, it yields pure oxide of nickel. The filtered solution contains all the cobalt in the form of cobalticyanide of potassium. It is supersaturated with acetic acid, boiled with sulphate of copper, which precipitates the cobalt in the form of cobalticyanide of copper ($Cu_3Co_2Cy_6.7HO$), and the precipitate retained in the liquid at a boiling-heat till it has lost its glutinous character. It is then washed, dried, and ignited, dissolved in hydrochloric acid mixed with a little nitric acid, the copper precipitated by hydrosulphuric acid, and the filtrate, after boiling for a minute to expel the excess of that gas, mixed with boiling caustic potash to precipitate the cobalt.*—2. Instead of adding the oxide of mercury, the solution containing the mixed cyanides may, after cooling, be supersaturated with chlorine, the precipitate of cyanide of nickel thereby produced being continually redissolved by caustic potash or soda. The chlorine produces no change on the cobalticyanide of potassium, but decomposes the nickel-compound, the whole of the nickel being ultimately precipitated in the form of black sesquioxide.*

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* Ann Ch. Pharm. lxv. 244.

Liebig's first method† which consisted in treating the solution of the mixed cyanides with excess of hydrochloric or sulphuric acid, whereby the nickel was precipitated as cobalticyanide of nickel, leaving a solution of pure cobalticyanide of potassium, has been found, both by himself and others, not to give perfectly satisfactory results. The method by oxalic acid (p. 75.), and the precipitation of nickel from an ammoniacal solution of the two metals by potash (p. 76.) are not sufficiently accurate for quantitative analysis.

F. Claudet proposes to separate cobalt from nickel and other metals in the form of the ammonio-compound described on page 70., that compound being very insoluble, while corresponding compounds of the other metals do not appear to be formed under the same circumstances.

The separation of cobalt from nickel (also from zinc and the previously described metals) may likewise be effected by means of St. Evre's yellow compound, which is regarded by A. Stromeyer as a nitrite of cobaltic oxide and potash (p. 65.). The solution containing the mixed metals is diluted with water till about 300 parts of water are present to 1 part of protoxide of cobalt; a somewhat concentrated solution of nitrite of potash ‡ then added, and a sufficient quantity of acetic acid to redissolve any precipitated carbonates; and the solution left to stand for 12 to 24 hours in a covered vessel, then filtered and washed, first with acetate of potash, afterwards with alcohol. The precipitate contains all the cobalt in the form of the above-mentioned salts, and none of the other metals.*

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* Ann. Ch. Pharm. lxxxvii. 128.

† Ibid. xli. 291.

‡ The nitrite of potash is prepared by fusing 1 part of nitre in contact with 2 parts of metallic lead, first at a low and then at a bright-red heat, exhausting the cooled mass with water, precipitating a small quantity of lead by carbonic acid, and then by sulphide of ammonium, evaporating to dryness, and heating to the melting-point to decompose any hyposulphite of potash that may have been formed.

SECTION V.

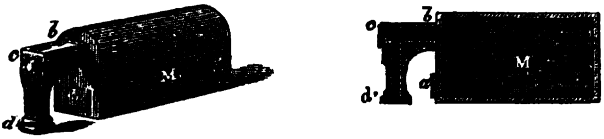
ZINC.

32·52; Zn. *or* *Eq.* 406·6.

The principal ores of zinc are *calamine*, or the carbonate, a pulverulent mineral generally of a reddish or flesh colour, and *zinc-blende*, a massive mineral of an adamantine lustre, and often black. The oxide, from the carbonate or from the calcined sulphide, is mixed with about $\frac{3}{4}$ of its weight of carbonaceous matter, and heated to a low white heat in retorts, or similar vessels of earthenware or iron. The zinc is then reduced and volatilised, and condenses in the colder part of the apparatus.

In Silesia, the mixture of zinc-oxide and charcoal, or coke, is heated in muffles (Fig. 4.) 3 feet long and 18 inches high, six of which are laid in one furnace (Fig. 5.), three side by side. The evolved mixture of carbonic oxide and zinc-vapour passes from the upper and fore part of the muffles M, through

Fig. 4.



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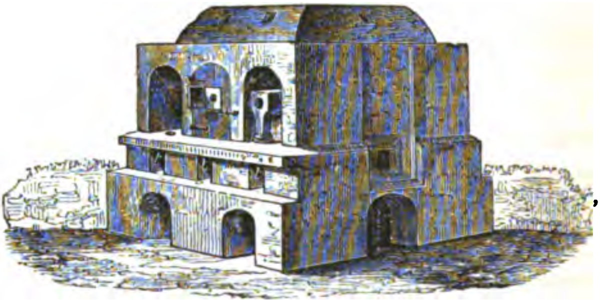
* A. Stromeyer, Ann. Ch. Pharm. xcvi. p. 218.; see also Liebig and Kopp's Jahresbericht, 1854, p. 357.

a knee-shaped channel *b c d,* and the zinc condenses therein and drops down from the lower aperture *d* into the reservoirs *t* (Fig. 5.) placed beneath.

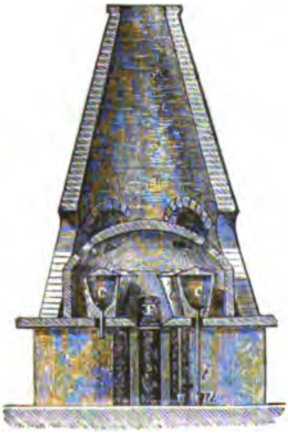
Fig. 5.



Part of the zinc-vapour, and likewise some cadmium-vapour, escapes uncondensed, together with the carbonic oxide gas, and burns in the air, producing the substance called *Silesian zinc-flowers.* Silesia furnishes the greater part of the zinc used in the arts.

In Belgium, the reduction is performed in earthenware tubes, laid side by side; and the zinc as it condenses in the fore part of these tubes, is scraped out from time to time in the liquid state.

Fig. 6.



In England, a number of cast-iron pots are arranged in a circle in the furnace (Fig. 6.). Through the bottom of each of these pots, there passes an iron tube *t t′*, which is continued downwards through an aperture in the bottom of the furnace. The upper end of the tube is stopped with a plug of wood, which is charred during the operation, and becomes sufficiently porous to allow the passage of the zinc-vapour, but at the same time prevents the solid matter from falling through. Each pot is fitted with a cover well luted with clay. The fire-place F, is in the middle. The distilled zinc condenses in the tubes *t t′*, and falls in drops into a receiver *u*, placed beneath. This process is called *destillatio per descensum*.

Zinc may be purified by a second distillation in a porcelain retort; but the first portions of that metal which come over should be rejected, as they generally contain cadmium and arsenic.

Zinc is a white metal, with a shade of blue, capable of being polished and then assuming a bright metallic lustre. It is usually brittle, and its fracture exhibits a crystalline structure. But zinc, if pure, may be hammered into thin leaves, at the usual temperature; and commercial zinc, which is impure and brittle at a low temperature, acquires the same malleability between 210° and 300°: it may then be laminated; and the metal is now consumed in the form of sheet zinc for a variety of useful purposes. At 400° it again becomes brittle, and may be reduced to powder in a mortar of that temperature. The density of cast zinc is 6·862, but it may be increased by forging to 7·21. Its point of fusion is 773° (Daniell). At a red heat, zinc rises in vapour and takes fire in the air, burning with a white flame like that of phosphorus; the white oxide produced is carried up mechanically in the air, although itself a fixed substance. Laminated zinc is a valuable substance, from its little disposition to undergo oxidation. When exposed to air or placed in water, its surface becomes covered with a grey film of suboxide, which does not increase; this film is better calculated to resist both the mechanical and chemical effects of other bodies than the metal itself, and preserves it. Zinc dissolves with facility in dilute hydrochloric, sulphuric and other hydrated acids, by substitution for hydrogen. In contact with iron, it protects the latter from oxidation in any saline fluid.

Zinc appears to form three oxides, the suboxide above referred to, the protoxide, and a peroxide, which last is produced when the hydrated protoxide is acted upon by a solution of peroxide of hydrogen; but of these, the first and last have not been studied, and the protoxide is, therefore, the only well known oxide of zinc.

Protoxide of zinc; ZnO; 40·52 *or* 506·6.—This oxide may be obtained, in the form of an anhydrous white powder, by the combustion of the metal in a stoneware crucible, or as a white hydrate, by precipitation from its salts by an alkali. It is of a yellow colour at high temperatures, but becomes colourless again on cooling. By the oxidation of zinc in air and water, without access of carbonic acid, a hydrate, $3ZnO + HO$, has been obtained in crystalline needles (Mitscherlich).

Oxide of zinc combines with acids and forms salts, which are colourless, like those of magnesia. *Caustic alkalies* form with zinc-salts a white gelatinous precipitate of the hydrated oxide, soluble in excess of the alkali. *Carbonate of potash* or *soda* throws down white carbonate of zinc, insoluble in excess; *carbonate of ammonia,* the same precipitate, soluble in excess. *Ferrocyanide of potassium,* and the *alkaline phosphates* and *arseniates,* also form white precipitates. Zinc-salts containing a strong acid in excess, are not affected by hydrosulphuric acid, but give a white hydrated sulphide with *alkaline sulphides.* A solution of acetate of zinc is readily decomposed by hydrosulphuric acid.

The native *sulphide of zinc,* or *zinc-blende,* ZnS, crystallises in octohedrons. Its colour is variable, being sometimes yellow, red, brown, or black.

Chloride of zinc, $ZnCl$, is produced by the combustion of zinc in chlorine, and by dissolving the metal in hydrochloric acid. It is fusible at 212°, volatile at a red heat, and perhaps the most deliquescent of salts. *Chloride of zinc-ammonium,*

$NH_3Zn.Cl$, is obtained, according to Ritthausen, in white prismatic crystals, when zinc and copper, or zinc and silver, are placed in contact in a solution of sal-ammoniac, or by the action of zinc on a solution of sal-ammoniac containing chloride of copper.

Iodide of zinc is formed by digesting iodine, zinc, and water together, and resembles the chloride. The compound $ZnI.2NH_3$, or $N\overbrace{H_2(NH_4)}Zn.I$, forms crystals belonging to the rhombic system (Rammelsberg).

The neutral *carbonate of zinc* forms the ore called calamine. When precipitated by an alkaline carbonate, the salts of zinc, like those of magnesia, yield the neutral carbonate in combination with hydrated oxide, $2(ZnO.CO_2) + 3(ZnO.HO)$. The mineral substance, *zinc-bloom*, is of the same composition. Precipitated in the cold, the carbonate is $ZnO.CO_2 + 2(ZnO.HO)$, but is contaminated with sulphate of soda (Mitscherlich).

Sulphate of zinc, White vitriol, $ZnO.SO_3 + 7HO$.—This salt is formed by the oxidation of the native sulphide at high temperatures, or by dissolving the metal in dilute sulphuric acid. It crystallises in colourless prismatic crystals, containing 7 eq. of water, the form of which is a right rhombic prism. This, like all the other magnesian sulphates, gives up 6 eq. of its water at about 212°, while the seventh or constitutional equivalent requires a heat of 400° to expel it. The crystals are soluble in 2½ times their weight of water, at the usual temperature, and fuse in their water of crystallisation when heated. The salt also crystallises above 86°, with 6 eq. of water, in oblique rhombic prisms (Mitscherlich). According to Kühn, another hydrate is formed and precipitated as a white powder, containing 2 eq. of water, when a concentrated solution of sulphate of zinc is mixed with oil of vitriol. Sulphate of zinc forms the usual double salt with sulphate of potash, $ZnO.SO_3 + KO.SO_3 + 6HO$. The double sulphate of zinc and soda contains 4 atoms of water, $ZnO.SO_3+NaO.SO_3+4HO$. It is formed by a singular decomposition (I. 228.). When a solution of the sulphate is mixed with a quantity of alkali less than sufficient for complete precipitation, a *subsulphate of zinc* precipitates, which, according to the analyses of several chemists, contains 4 eq. of oxide of zinc to 1 eq. of sulphuric acid, besides water. A concentrated solution of sulphate of zinc dissolves the preceding subsalt, and, when saturated, contains a compound of 1 eq. of acid and 2 eq. of base, according to Schindler, and does not crystallise. From this solution, Schindler obtained the former insoluble subsalt with two different proportions of water, in long crystalline needles, containing 10HO, by spontaneous evaporation of the solution, and in brilliant crystalline plates containing 2HO, which were deposited on boiling the solution. By diluting the same solution with a large quantity of water, he also obtained another subsalt, as a light bulky precipitate, which contained 1 eq. of acid, 8 eq. of oxide of zinc, and 2 eq. of water. The insoluble matter, which precipitates when sulphate of zinc-ammonium $(NH_3Zn)O.SO_3$ is thrown into water, is considered by Kane as a third subsulphate of zinc, containing 1 eq. of acid, 6 eq. of oxide of zinc, and 10 eq. of water. All these subsulphates afford neutral sulphate of zinc to water, after being heated to redness; so that, whatever their constitution may be when hydrated, it is certainly different from what it is in their anhydrous condition.

Nitrate of zinc, $ZnO.NO_5+6HO$, is very soluble in water, and moderately deliquescent.

Phosphate of zinc, $ZnO_2.HO.PO_5 + 2HO$, is obtained in minute silvery plates, which are nearly insoluble, on mixing dilute solutions of phosphate of soda and sulphate of zinc.

Silicate of zinc is found as a crystalline mineral, which has received the name of the electrical oxide of zinc, because it acquires, like the tourmalin, a high degree of electrical polarity when heated. It contains water, and may be represented by the formula $2(3ZnO.SiO_3)+3HO$.

The most important *alloys of zinc* are those with copper, which form the varieties of brass. Zinc also combines readily with iron, and is contaminated by that metal, when fused in an iron crucible.

ESTIMATION OF ZINC, AND METHODS OF SEPARATING IT FROM OTHER METALS.

Zinc is precipitated from its solutions by carbonate of soda, which, when added in excess and boiled with the solution, throws down carbonate of zinc. It is best, however, to pour the zinc-solution into the hot solution of the alkaline carbonate, because, in that case, we may be sure of not forming a basic salt. If the zinc-solution contains ammoniacal salts, it must be boiled with a quantity of carbonate of soda sufficient to decompose those salts; then evaporated to dryness; the residue treated with a large quantity of water to dissolve out the soluble salts; and the carbonate of zinc collected on a filter and well washed with hot water. The evaporation should be conducted as quickly as possible. The carbonate of zinc, when dried and ignited, yields oxide of zinc containing 80·26 per cent. of the metal.

In separating zinc from other metals, it is often necessary to precipitate by sulphide of ammonium. If the solution is acid, it must be previously neutralised by ammonia. The precipitate must not be thrown on the filter immediately, but left to settle down completely, after which the clear liquid must first be passed through the filter, and then the precipitate thrown on it. If this precaution be neglected, the sulphide of zinc will stop up the pores of the filter. The precipitate is washed with water containing a little sulphide of ammonium; then dissolved in hydrochloric acid; the solution boiled to drive off the hydrosulphuric acid; and the zinc precipitated by carbonate of soda as above.

Zinc is separated from the *alkalies* and *alkaline earths* (baryta, strontia, and lime) by means of sulphide of ammonium. In the case of the alkaline earths, however, great care must be taken to prevent the ammoniacal liquid from absorbing carbonic acid from the air, as that would occasion a precipitation of the earth in the form of carbonate. For this purpose, the filtration must be effected as quickly as possible, and the liquid well protected from the air. The separation of zinc from *baryta* may also be effected by sulphuric acid, and from *lime* by oxalate of ammonia.

From *magnesia*, zinc may be separated by sulphide of ammonium, a sufficient quantity of chloride of ammonium being previously added to prevent the precipitation of the magnesia. Or the separation may be effected by converting the zinc and magnesia into acetates, and precipitating the zinc as sulphide by hydrosulphuric acid.

The separation of zinc from *alumina* and *glucina* may also be effected by converting the two bases into acetates and precipitating the zinc by hydrosulphuric acid; or by dissolving in potash, and precipitating the zinc by hydrosulphuric acid; but the former method is to be preferred.

The conversion into acetates and precipitation by hydrosulphuric acid likewise serves to separate zinc from *zirconia, yttria, thorina,* and *manganese*. The separation from manganese may also be effected by converting the two metals into chlorides, passing chlorine gas through the solution to convert the manganese into bioxide, and completing the precipitation of the latter by carbonate of baryta.

From *iron,* zinc may be separated by ammonia, or better by succinate of ammonia, the same precautions being used as in the separation of iron from manganese by the same method (p. 58.). The iron (in the state of sesquioxide) may also be precipitated by carbonate of lime or carbonate of baryta.

From *cobalt* and *nickel*, zinc is separated by dissolving the oxides of both metals in *excess* of acetic acid, and precipitating the zinc by hydrosulphuric acid. Nickel and cobalt are completely precipitated by hydrosulphuric acid from the neutral solutions of their acetates, but not when a considerable excess of acetic acid is present. But in separating zinc from cobalt and nickel in this manner, a small quantity of the latter metals is generally precipitated with the zinc towards the end of the process, the precipitate then becoming greyish black. In that case it must be redissolved in hydrochloric acid, the chlorides converted into acetates, and the precipitation repeated. Another method of separation is to convert the metals into chlorides, and ignite the dry chlorides in a stream of hydrogen gas: the nickel or cobalt is then reduced to the metallic state, while the chloride of zinc remains unaltered, and may be dissolved out by water. (For the separation of cobalt from zinc, see also p. 80.)

In precipitating zinc from its acetic acid solution by hydrosulphuric acid, it is necessary that the solution be quite free from inorganic acids, which would interfere with the precipitation. This may be effected either by precipitating the metals with carbonate of soda, washing the precipitate and dissolving it in acetic acid, or by boiling the solution with excess of sulphuric acid to drive off the inorganic acids (if volatile) and decomposing the sulphate with acetate of baryta.

SECTION VI.

CADMIUM.

Eq. 55·74 *or* 696·77; Cd.

This metal is frequently found in small quantity, associated with zinc, and derives the name cadmium, applied to it by Stromeyer, from *cadmia fossilis*, a denomination by which the common ore of zinc was formerly designated. In the process of reducing ores of zinc, the cadmium which they contain comes over among the first products of distillation, owing to its greater volatility. It may be separated from zinc, in an acid solution, by hydrosulphuric acid, which throws down cadmium as a yellow sulphide. This sulphide dissolves in concentrated hydrochloric acid, affording the chloride of cadmium, from which the carbonate may be precipitated by an excess of carbonate of ammonia. Carbonate of cadmium is converted by ignition into the oxide; and the latter yields the metal when mixed with one-tenth of its weight of pounded coal, and distilled in a glass or porcelain retort, at a low red heat.

Cadmium is a white metal, like tin, very ductile and malleable. It fuses considerably under a red heat, and is nearly as volatile as mercury. The density of cadmium, cast in a mould, is 8·604, after being hammered, 8·6944. Cadmium may be dissolved in the more powerful acids, by substitution for hydrogen, with the aid of heat; but nitric acid is its proper solvent.

Oxide of cadmium, CdO; 63·74 *or* 796·77.—The only known oxide of cadmium is obtained by the combustion of the metal, or by the ignition of its carbonate, as a powder of an orange colour, or as a white hydrate by precipitation from its salts by an alkali. Its density, in the anhydrous condition, is 8·183 (Herapath). By igniting the nitrate, the oxide is obtained in microscopic octohedrons, which are dark bluish black by reflected, and dark brown with a tinge of violet by transmitted light (Schüler). This oxide is soluble in ammonia, but not in its carbonate (differing in the last property from zinc and copper) nor in the fixed alkalies. Its salts are white, and greatly resemble those of zinc. They are precipitated of a fine yellow colour by hydrosulphuric acid.

Sulphide of cadmium is distinguished from sulphide of arsenic, which it resembles in colour, by being insoluble in potash and in sulphide of ammonium, and by sustaining a red heat without subliming. A crystalline sulphide is obtained by fusing 1 part of the precipitated sulphide with 5 parts of carbonate of potash and 5 parts of sulphur; or by passing dry hydrosulphuric acid gas over strongly-heated chloride of cadmium.

Chloride of cadmium forms a crystalline hydrate, containing $CdCl + 2HO$. It also forms crystalline compounds with the chlorides of ammonium, potassium, sodium, barium, strontium, calcium, magnesium, manganese, iron, cobalt, nickel, and copper. A solution of chloride of cadmium, mixed with excess of ammonia, yields by spontaneous evaporation the compound NH_2CdCl (C. v. Hauer).

The same ammoniacal solution treated with excess of hydrochloric acid deposits crystalline crusts, which, according to Schüler, contain $CdCl.3NH_3$ or $N\overbrace{H(NH_4)_2Cd}.Cl$. Sulphurous acid gas passed through the ammoniacal solution throws down a white crystalline precipitate containing $CdO.SO_2 + NH_4O.SO_2$ (Schüler).

Iodide of cadmium forms a crystalline compound with water.

Bromide of cadmium mixed in equivalent quantity with bromide of potassium in solution, yields crystals, first of $2CdBr.KBr + 2HO$, afterwards of $CdBr.2KBr$ (C. v. Hauer).

Sulphate of cadmium forms efflorescent crystals containing $CdO.SO_3 + 4HO$ (Stromeyer). According to Kühn and Von Hauer, an acid solution of the salt concentrated at the boiling heat, deposits nodular crystals, which contain $CdO.SO_3 + HO$, and give off their water at 212°. The crystals obtained by evaporation at ordinary temperatures contain $3(CdO.SO_3) + 8HO$, give off nearly 3 eq. water at 212°, and the rest at a low red heat (C. v. Hauer). Sulphate of cadmium forms with sulphate of potash the compound $CdO.SO_3 + KO.SO_3 + 6HO$, and similar double salts with the sulphates of soda and ammonia.

Several definite *alloys of cadmium* have been formed. At a red heat, 100 parts of platinum retain 117·3 parts of cadmium, giving a compound = Cd_2Pt: 100 parts of copper retain, at a red heat, 82·2 of cadmium, which approaches nearly to the proportion of $CdCu_2$. Cadmium forms an amalgam with mercury, which crystallises in octohedrons, and consists of 21·74 parts of cadmium, and 78·26 of mercury, Cor dHg_2.

Estimation of cadmium, and method of separating it from the preceding metals. — Cadmium is best precipitated from its solutions by carbonate of soda; it is thereby obtained as a carbonate, which by ignition yields the brown oxide containing 87·45 per cent. of the metal.

From all the preceding metals cadmium may be separated by hydrosulphuric acid; the sulphide of cadmium being then dissolved by nitric acid, and the metal precipitated by carbonate of soda as above.

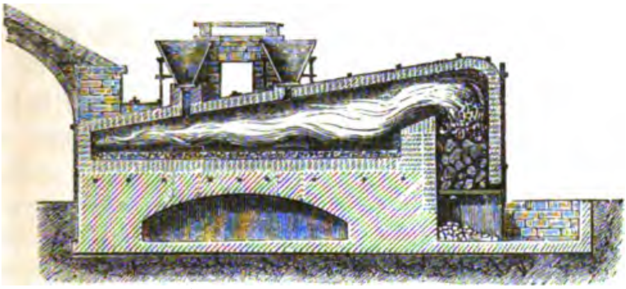
SECTION VII.

COPPER.

Eq. 31·66 *or* 395·7; Cu (*cuprum*).

Copper, if not the most abundant, is certainly one of the most generally diffused of the metals. Its ores are often accompanied by metallic copper, crystallised in cubes or octohedrons. Very large masses of native copper have been found near Lake Superior in North America, one of which weighed 2200 pounds; in the Cliff mine, on the Eagle river, a mass has been found weighing 50 tons. Native copper is also found in considerable quantities in the decomposed basalt of Rheinbreitenbach, near Recsk in Hungary, and near Harlech, North Wales. The richest mines of this country are those in Cornwall and Anglesea. The common ore of this metal is *copper pyrites,* a compound of subsulphide of copper and sesquisulphide of iron, or a sulphur-salt, $CuS + Fe_2S_3$, but in which the two sulphides are also found in other proportions, and which often contains an admixture of the bisulphide of iron. Few metallurgic processes require more skill and attention than the extraction of copper from this ore. The ore is first roasted at a high temperature in a reverberatory or flame-furnace (Fig. 7.), whereby the sulphide of iron is in great part converted into oxide, while the sulphide of copper remains unaltered. The product of this operation is then strongly heated with silicious sand, which combines with the oxide of iron, forming a fusible slag, and separates from the heavier copper compound. This operation is performed in a reverberatory furnace similar to the former, but of smaller dimensions. These processes are several times repeated, whereby the quantity of iron is continually diminished, and the sulphide of copper begins to decompose, giving it up its sulphur and absorbing oxygen; the temperature is then raised high enough to reduce the resulting oxide by the aid of carbonaceous matter. The *coarse copper* thus obtained, containing from 80 to 90 per cent. of copper, is then melted under the action of a strong blast of air, to complete the expulsion of volatile matter, and the copper is partially oxidised. Lastly, to free it from oxide, which renders it brittle, it is again melted with its surface well covered with charcoal, and a pole of birchwood is thrust into it; this causes considerable ebullition, the oxide being reduced

Fig. 7.



by the carbonaceous matter, and carbonic acid escaping. Samples of the metal are taken out from time to time, and tested by the hammer, the process being discontinued as soon as the right degree of toughness is attained. If the *poling* is continued too long, the copper takes up carbon, and then becomes even more brittle than in its former oxidised state: it is then said to be *over-poled,* and must be again melted in contact with the air to burn away the carbon.*

Copper is the only metal of a red colour. The crystals of native copper, and of that obtained in the humid way by precipitation with iron, belong to the regular system; but the crystals which form in the cooling of melted copper were found by Seebeck to be rhomboïdal, and to have a different place in the thermo-electric series from the other crystals. The density of copper when cast is about 8·83, and when laminated or forged 8·95 (Berzelius). It is less fusible than silver, but more so than gold, its point of fusion being 1996° (Daniell). It is one of the most highly malleable metals, and in tenacity is inferior only to iron. It has much less affinity for oxygen than iron, and decomposes water only at a bright red heat, and to a small extent. In damp air, it acquires a green coating of subcarbonate of copper, and its oxidation is remarkably promoted by the presence of acids. The weaker acids, such as acetic, have no effect upon copper, unless with the concurrence of the oxygen of the air, when the copper rapidly combines with that oxygen, and a salt of the acid is formed. Copper scarcely decomposes the hydrated acids by displacing hydrogen; when boiled in hydrochloric acid, it disengages only the smallest traces of that gas. But hydrogen does not precipitate metallic copper from solution. Copper acts violently on nitric acid, occasioning its decomposition, with evolution of nitric oxide, and dissolving as a nitrate.

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* A minute account of the process of copper-smelting as practised at Swansea, has lately been given by Mr. Napier, in the "Philosophical Magazine," 4th Series, vols. iv. and v.

Dioxide of copper, Red oxide of copper, Cuprous oxide, Cu_2O; 71·32 or 891·4.—This degree of oxidation is better marked in copper than in any other metal of the magnesian class. The dioxide of copper is found native in octohedral crystals, and may be prepared artificially by heating to redness, in a covered crucible, a mixture of 5 parts of the black oxide of copper with 4 parts of copper-filings. It is a reddish-brown powder, which undergoes no change in the air. The surface of vessels of polished copper is often converted into red oxide, or bronzed, to enable them to resist the action of air and moisture: this is done by covering them with a paste of sesquioxide of iron, heating to a certain point, and afterwards cleaning them, to remove the oxide of iron; or otherwise, by means of a boiling solution of acetate of copper.

Dilute acids decompose red oxide of copper, dissolving the protoxide, and leaving metallic copper. Undiluted hydrochloric acid dissolves the red oxide, without decomposition, or rather forms a corresponding chloride of copper, Cu_2Cl, which is soluble in hydrochloric acid. The hydrated alkalies precipitate hydrated cuprous oxide from that solution, of a lively yellow colour, which changes rapidly in air from absorption of oxygen.

Cuprous oxide is also formed when copper is placed in a dilute solution of ammonia containing air, and is dissolved by the alkali. If the ammonia has been corked up in a bottle with copper for some time, the liquid is colourless; but on pouring it out in a thin stream, it immediately becomes blue, by absorbing oxygen. The liquid may be again deprived of colour by returning it to the bottle, and closing it up, in contact with the metal. Cuprous oxide is also readily obtained by the reducing action of glucose (grape-sugar) on the protoxide or its salts. When a solution of 1 part of common sulphate of copper and 1 part of glucose is mixed with a sufficient quantity of caustic potash or soda to redissolve the precipitate first formed, and the liquid gently warmed, cuprous oxide is abundantly precipitated in the form of a yellowish-red crystalline powder. Cane-sugar produces the same effects, but more slowly, apparently because it must first be converted into glucose.

Compounds have been obtained of cuprous-oxide with several acids, particularly with sulphurous acid, the sulphite forming a double salt with sulphite of potash, $Cu_2O.SO_2 + 2(KO.SO_2)$ (Muspratt); also with hyposulphurous, sulphuric, carbonic and acetic acids. When fused with vitreous matter, cuprous oxide gives a beautiful ruby-red glass; but it is difficult to prevent the cuprous oxide from absorbing oxygen, in which case the glass becomes green.

Hydride of copper, Cuprous hydride, Cu_2H. — When a solution of cupricsulphate and hypophosphorous acid is heated not above 158°, this compound is deposited as a yellow precipitate, which soon turns red-brown. It gives off hydrogen when heated, takes fire in chlorine gas, and when treated with hydrochloric acid, is converted into dichloride of copper, with evolution of a double quantity of hydrogen, the acid in fact giving up its hydrogen as well as the copper-compound (Wurtz):

$$Cu_2H + HCl = Cu_2Cl + HH.$$

This action is very remarkable, inasmuch as metallic copper is scarcely acted upon by hydrochloric acid. It appears to arise from the two atoms of hydrogen contained in the acid and the hydride being in opposite states, the former being basylous or positive, the latter chlorous or negative, and so disposed to *combine together,* just as the hydrogen of the hydrochloric acid combines under similar circumstances with the oxygen of the compound Cu_2O. The reduction of certain metallic oxides by peroxide of hydrogen affords another example of the same kind of action.

Disulphide of copper, Cuprous sulphide, Cu_2S, forms the mineral *copper-glance,* and is also a constituent of copper pyrites. It is a powerful sulphur-base. Copper-filings, mixed with half their weight of sulphur, unite, when heated, with intense ignition, and form this disulphide.

Dichloride of copper, Cuprous chloride, Cu_2Cl, may be prepared by heating copper-filings with twice their weight of corrosive sublimate. It was obtained by Mitscherlich in tetrahedrons, by dissolving in hydrochloric acid the dichloride of copper formed on mixing solutions of the protochlorides of copper and tin, and allowing the concentrated solution to cool. Dichloride of copper so prepared is white, insoluble in water, soluble in hydrochloric acid, but precipitated by dilution. It is dissolved by a boiling solution of chloride of potassium, and the resulting solution, if allowed to cool in a close vessel, yields large octohedral crystals of a double chloride: $Cu_2Cl.2KCl$; they are anhydrous. It is remarkable that the forms of this double salt, and of both its constituents, all belong to the regular system.*

When finely-divided metallic copper is boiled in a saturated solution of sal-ammoniac, ammonia is evolved and a white salt formed, which crystallises in rhombic dodecahedrons: it contains $NH_3.Cu_2Cl$, and may be regarded as a dichloride of copper and cuprammonium $\left.\begin{matrix}NH_3Cu\\Cu\end{matrix}\right\}Cl$. A solution of this salt exposed to the air yields blue crystals of the compound $NH_3.Cu_2Cl + NH_3CuCl + HO$; and the mother-liquor, after further exposure to the air, contains the salt $NH_3.CuCl + NH_4Cl$, which at a lower temperature crystallises in large cubes (Ritthausen).

Diniodide of copper, Cuprous iodide, Cu_2I, is a white insoluble precipitate, obtained on mixing a solution of 1 part of sulphate of copper and $2\frac{1}{4}$ parts of protosulphate of iron, with a solution of iodide of potassium.

Dicyanide of copper, Cuprous cyanide, Cu_2Cy.—Obtained as a white curdy precipitate on adding hydrocyanic acid or cyanide of potassium to a solution of dichloride of copper in hydrochloric acid, or to a solution of protochloride of copper mixed with sulphurous acid. It forms a colourless solution with ammonia, and a yellow solution with strong hydrochloric acid, from which it is precipitated by potash.

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* Mitscherlich in Poggendorff's Annalen, xlix. 401., 1840.

Dicyanide of copper unites with the cyanides of the alkali- and earth-metals, and with the cyanides of manganese, iron, zinc, cadmium, lead, tin, uranium, and silver, forming double salts, some of which have the composition $MCy.Cu_2Cy$, others $3MCy.Cu_2Cy$ (the symbol M denoting a metal).

Cuproso-cupric cyanide, $Cu_2Cy.CuCy$, is obtained as a green hydrate by adding hydrocyanic acid or cuproso-potassic cyanide, $KCy.Cu_2Cy$, to sulphate of copper. It forms three compounds with ammonia, viz., $NH_3.Cu_3Cy_2.HO$, obtained by adding cyanide of ammonium to a protosalt of copper, and the compounds $2NH_3.Cu_3Cy_2$ and $3NH_3.Cu_3Cy_2$, formed by the action of ammonia on the first compound.

Cuprous hyposulphite, $Cu_2O.3S_2O_2 + 2HO$, separates in microscopic needles, having a golden lustre, on adding a saturated solution of hyposulphite of soda to a concentrated solution of cupric sulphite, till a deep yellow colour is produced. It dissolves in aqueous sal-ammoniac, and the solution deposits the compound $Cu_2O.3S_2O_2 + NH_3CuCl + HO$. (C. v. Hauer).

Cuprous sulphite is said by some chemists to be obtained in a definite state by the action of sulphurous acid on cupric oxide; but according to Rammelsberg and Péan de St. Gilles, it exists only in combination with cupric sulphite, forming the compound $Cu_2O.SO_2 + CuO.SO_2$, which crystallises with 3 and 5 eq. of water,—and with the sulphites of the alkalies. By treating dichloride of copper with excess of sulphite of ammonia, prismatic crystals are formed containing $Cu_2O.SO_2 + 7(NH_4O.SO_2) + 10$ Aq.; and by saturating the solution of this salt with sulphurous acid, the salt $Cu_2O.S_2O_2 + NH_4O.SO_3$ is obtained. A concentrated solution of sulphite of ammonia and cupric sulphate saturated with sulphurous acid gas, yields light green crystals containing $(Cu_2O.SO_2 + NH_4O.SO_2) + (Cu_2O.SO_2 + CuO.SO_2) + 5$ aq. Corresponding double salts are formed by the sulphites of potash and soda, but they are very unstable.

Protoxide of copper, Black oxide of copper, Cupric oxide, CuO; 495·7 or 39·66.—The base of the ordinary salts of copper, or cupric salts. It is formed by the oxidation of copper at a red heat, but is generally prepared by igniting the nitrate of copper. It is black like charcoal, and fuses at a high temperature. This oxide is remarkable for the facility with which it is reduced, at a low red heat, by hydrogen and carbon, which it converts into water and carbonic acid. It is this property which recommends oxide of copper for the combustion of organic substances, in close vessels, by which their ultimate analysis is effected.

Oxide of copper is a powerful base. Its salts, the *cupric salts*, are generally blue or green, when hydrated, but white when anhydrous. Although neutral in composition, they have a strong acid reaction. They are poisonous; but their effect upon the animal system is counteracted in some degree by sugar. Liquid albumen forms insoluble compounds with these salts, and is an antidote to their poisonous action. Copper is separated in the metallic state from its salts by zinc, iron, lead, and the more oxidable metals, which are dissolved, and take the place of the former metal.

Potash or *soda* added to the solution of a cupric salt, throws down at first a blue precipitate of hydrated cupric oxide, which, however, on agitation, takes up a portion of the undecomposed salt, and forms with it a green basic salt. An excess of the alkali throws down the hydrated oxide in bulky blue flakes, which, on boiling the mixture, collect together in the form of a black powder, consisting of the anhydrous oxide. This reaction is greatly modified by the presence of fixed organic substances, such as sugar, tartaric acid, &c. In a solution of sulphate of copper, containing such substances in sufficient quantity, potash either produces no precipitate, or one which is quickly redissolved, forming a blue solution; and from this solution, when boiled, the copper is sometimes wholly precipitated as red or yellow cuprous oxide, as when grape-sugar is present,—or partially, as with cane-sugar, or not at all, as with tartaric acid. *Ammonia*, added by degrees, and with constant agitation, to the solution of a cupric salt, first throws down a green basic salt, and afterwards the blue hydrate: an excess of ammonia dissolves the precipitate, forming a deep blue solution. A copper solution diluted so far as to be colourless, becomes distinctly blue on the addition of ammonia. The blue colour thus produced is still visible, according to Lassaigne, in a solution containing 1 part of copper in 100,000 parts of liquid. *Carbonate of potash* or *soda* throws down, with evolution of carbonic acid, a greenish blue precipitate of a basic carbonate of copper, which on boiling is converted into the black oxide. *Carbonate of ammonia* produces the same precipitate, but when added in excess, dissolves it abundantly, forming a blue solution. *Hydrosulphuric acid* and solutions of *alkaline sulphides* throw down a brownish black precipitate of protosulphide of copper, insoluble in sulphide of potassium or sodium, slightly soluble in sulphide of ammonium. *Ferrocyanide of potassium* forms with cupric salts a deep chocolate-coloured precipitate of ferrocyanide of copper. To very dilute solutions it imparts a reddish colour, which is even more delicate in its indications than the ammonia reaction, being still visible in a solution containing 1 part of copper in 400,000 parts of liquid, according to Lassaigne, and in 1,000,000 parts, according to Sarzeau. Ferrocyanide of copper dissolves in aqueous ammonia, and reappears when the ammonia is evaporated. This reaction serves to detect extremely small quantities of copper, even when associated with other metals. Thus, if a solution containing copper and iron be treated with excess of ammonia, a few drops of ferrocyanide of potassium added, the liquid filtered, and the filtrate left to evaporate in a small white porcelain capsule, ferrocyanide of copper will be left behind, exhibiting its characteristic red colour (Warington). Salts of copper impart a green colour to flame. The black oxide of copper dissolves by fusion in a vitreous flux, and produces a green glass. Any compound of copper fused with borax in the oxidising flame of the blowpipe forms a transparent glass, which is green while hot, but assumes a beautiful blue colour when cold. In the reducing flame, the glass becomes opaque, and covered on the surface with liver-coloured streaks of cuprous oxide, or metallic copper. This last reaction is somewhat difficult to obtain, especially when the quantity of copper is small, but it may always be ensured by fusing a small piece of metallic tin in the bead. Copper salts mixed with carbonate of soda or cyanide of potassium, and heated on charcoal before the blowpipe, yield metallic copper.

Thénard obtained a higher oxide of copper, CuO_2, by the action of diluted bioxide of hydrogen on the hydrated prot_ oxide of copper.

Chloride of copper, cupric chloride, CuCl, is obtained by dissolving the black oxide in hydrochloric acid. Its solution is green when concentrated, but blue when more dilute, and the salt forms blue prismatic crystals, containing two atoms of water. It combines with chloride of potassium, and more readily with chloride of ammonium, forming the double salts $KCl.CuCl + 2HO$, and $NH_4Cl.CuCl + 2HO$. Another chloride of copper and ammonium, containing $NH_4Cl.2CuCl + 4HO$, is obtained in fine bluish-green crystals, by mixing the solutions of 1 eq. sal-ammoniac and 2 eq. chloride of copper.

Chloride of copper likewise combines with ammonia, forming the three following compounds:—*a*. $3NH_3.CuCl$. This compound is obtained by saturating dry protochloride of copper with ammoniacal gas: it forms a blue powder.—*b*. $2NH_3.CuCl$. Formed by passing ammoniacal gas through a hot saturated solution of protochloride of copper, till the precipitate first formed is completely redissolved. During this process, the liquid is kept almost boiling by the heat developed by the absorption of the gas; and the resulting solution yields, on cooling, small dark blue octohedrons and square prisms with four-sided summits.—*c*. $NH_3.CuCl$. Obtained by heating *a* or *b* to 300°, or by saturating dry chloride of copper, at a high temperature, with ammoniacal gas. Forms a green powder. The compound *c* may also be regarded as *chloride of cuprammonium*, $NH_3Cu.Cl$, or *hydrochlorate of cupramine*, $NH_2Cu.HCl$, the base being ammonium or ammonia in which 1H is replaced by Cu. Similarly, *b* may be regarded as a *basic hydrochlorate of dicupramine*, $N_2H_5Cu.HCl$, the base being formed by the union of two atoms of ammonia into one, and the substitution therein of 1Cu for 1H. Lastly, *a* may be regarded as *basic hydrochlorate of tricupramine*, $N_3H_8Cu.HCl$; or again, *a* may be regarded as $N\overbrace{HAm_2Cu}.Cl$, and *b* as $N\overbrace{H_2AmCu}.Cl$.

Carbonates of copper.—When a salt of copper is precipitated by an alkaline carbonate, a hydrated subcarbonate is produced containing 2 eq. of oxide of copper to 1 eq. carbonic acid. It is a pale blue bulky precipitate, which becomes denser and green when treated with boiling water. It is used as a pigment, and known as *mineral green*. The beautiful native green carbonate of copper, *malachite*, is of the same composition, $CuO.CO_2 + CuO.HO$. The finely crystallised *blue copper ore* is another subcarbonate. It may be represented as the neutral hydrated carbonate of copper, in combination with a similar carbonate of copper, in which the constitutional water is replaced by oxide of copper:

$$\left\{\begin{array}{l}CuO.CO_2 + HO.\\ CuO.CO_2 + CuO.\end{array}\right.$$

In the green carbonate, the constitutional water of the neutral carbonate of copper is replaced by hydrate of copper. The neutral carbonate of copper itself, of which the formula would be $CuO.CO_2 + HO$, is unknown. According to Thomson*, the anhydrous subcarbonate $2CuO . CO_2$, occurs in the form of *mysorine*, which contains also ferric oxide and silica.

Sulphate of copper, Cupric sulphate, Blue vitriol, $CuO.SO_3 . HO + 4HO$; 79·66 *or* 995·7 + 562·5.—This salt may be formed by dissolving copper in sulphuric acid diluted with half its bulk of water, with ebullition; the metal is then oxidated with formation of sulphurous acid. But the sulphate of copper is more generally prepared, on the large scale, by the roasting and oxidation of sulphide of copper; or by dissolving in sulphuric acid the oxide formed by exposing sheets of metallic copper to air at a red heat. It forms large rhomboïdal crystals of a sapphire-blue colour, containing 5 eq. of water, which lose their transparency in dry air: they are soluble in four times their weight of cold, and twice their weight of boiling water. Like the other soluble salts of copper, the sulphate has an acid reaction; it is used as an escharotic. The water in this salt may be reduced to 1 eq. at 212°; above 400° the salt is anhydrous and white. Although sulphate of copper does not crystallise alone with 7HO, yet, when mixed with the sulphates of magnesia, zinc, nickel, and iron, it crystallises along with these isomorphous salts in the form of sulphate of iron. At a strong red heat it melts and loses acid.

The anhydrous sulphate absorbs 2½ eq. of ammonia, and forms a light powder of a deep blue colour (H. Rose). When ammonia is added to a solution of sulphate of copper, an insoluble subsulphate is first thrown down, which is redissolved as the addition of ammonia is continued, and the usual deep azure-blue ammoniacal solution formed. The ammoniacal sulphate may be obtained in beautiful indigo-blue crystals, by passing a stream of ammoniacal gas into a saturated hot solution of the sulphate: it is $CuO.SO_3.HO + 2NH_3$ (Berzelius). These crystals lose 1 eq. ammonia and 1 eq. water at 390° (Kane), and are converted into a green powder, $CuO.SO_3 + NH_3$, or $(NH_3CuO).SO_3$; by the cautious application of a heat not exceeding 500°, the whole of the ammonia may be got rid of, and sulphate of copper quite pure remains behind. Sulphate of copper forms the usual double salts with sulphate of potash and with sulphate of ammonia. A saturated hot solution of the double sulphate of copper and potash allows a remarkable double subsalt to precipitate in crystalline grains, $KO.SO_3 + 3(CuO.SO_3) + CuO.HO + 3HO$. A corresponding seleniate is deposited, below the boiling point, and always in crystals. The ammoniacal and double salts of sulphate of copper may be represented thus:—

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* Outlines of Mineralogy.

Sulphate of copper (blue vitriol) . . .	$CuO.SO_3,HO + 4HO$
Sulphate of copper and potash	$CuO.SO_3,(KO.SO_3) + 6HO$
Hydrated ammoniacal sulphate of copper	$CuO.SO_3,HO + 2NH_3$
Preceding salt dried at 300°	$(NH_3.CuO).SO_3$
Rose's ammoniacal sulphate	$CuO.SO_3 + (NH_3CuO)SO_3 + 4NH_3$
Do. heated to 350°	$CuO.SO_3 + (NH_3CuO)SO_3$

The hydrated ammoniacal sulphate may also be regarded as $NH_2\overbrace{(NH_4)Cu}.SO_4$; and Rose's ammoniacal sulphate as

$$\left.\begin{matrix} NH_2\overbrace{(NH_4)Cu} \\ NH\overbrace{(NH_4)_2Cu} \end{matrix}\right\} 2SO_4.$$

Several *subsulphates of copper* have been formed. By digesting hydrated oxide of copper in a solution of sulphate of copper, a green powder is obtained, of which the constituents are, according to Berzelius, $3CuO.SO_3 + 3HO$. The bluish-green precipitate which falls when ammonia is added to sulphate of copper, or potash added in moderate quantity to the same salt, contains, according to Kane's and Graham's analyses $4CuO.SO_3 + 4HO$. By a larger quantity of potash, Kane precipitated a clear grass-green subsulphate, containing

$8CuO.SO_3+12HO$. The last subsulphate loses exactly half its water at 300°.*

Nitrate of copper, $CuO.NO_5+3HO$, is formed by dissolving copper in nitric acid. It crystallises from a strong solution in blue prisms which contain 3 atoms of water, or in rhomboïdal plates which contain 6 atoms of water. This salt acts upon granulated tin, with nearly as much energy as hydrated nitric acid. A crystallised *ammoniacal nitrate of copper* is obtained by conducting a stream of ammoniacal gas into a saturated solution of nitrate of copper. It is anhydrous, and contains $NO_5.CuO + 2NH_3$ (Kane). It may be regarded as $N\overbrace{H_2(NH_4)Cu}.NO_6$.

Subnitrate of copper, $CuO.NO_5 + 3(CuO . HO)$, according to the analyses of Gerhardt, Gladstone†, and Kuhn‡, is a green powder, produced by the action of heat upon the neutral nitrate, at any temperature between 160° and 600°; or by adding to that salt a quantity of alkali insufficient for complete precipitation. When oxide of copper is drenched with the most concentrated nitric acid ($HO.NO_5$), it is this subsalt, singular as it may appear, which is formed, even when the acid is in great excess.

Oxalate of copper and potash is obtained by dissolving oxide of copper in binoxalate of potash; it crystallises with 2 and with 4 eq. of water.

Acetates of copper.—The *neutral acetate*, $CuO.(C_4H_3O_3)+HO$, or $C^4H^3CuO^4 + HO$, is obtained by dissolving oxide of copper in acetic acid. It forms fine crystals of a deep green colour, containing 1 eq. of water, which lose their transparency in air, and are soluble in 5 times their weight of boiling water. This salt, when it separates from an acid solution below 40°, also forms blue crystals containing 5HO

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[*] Transactions of the Royal Irish Academy, vol. xix. p. 1.; or Ann. Ch. Phys. t. lxxii. p. 272.

[†] Chem. Soc. Mem. iii. 480.

[‡] Arch. Pharm. [2.], l. 283.

(Wöhler). The green salt is found in commerce under the improper name of *distilled verdigris.* The acetates of copper and potash unite in single equivalents, and form a double salt in fine blue crystals, containing 8HO. *Verdigris* is a subacetate of copper, formed by placing plates of the metal in contact with the fermenting marc of the grape, or with cloth dipped in vinegar. The bluer species, which consists of minute crystalline plates, is a definite compound of 1 eq. acetic acid, 2 eq. oxide of copper, and 6 eq. of water, $C_4H_3CuO_4.CuO + 6HO$. The ordinary green species is a mixture of the sesqui- and tribasic acetates of copper, with the preceding bibasic acetate. Water dissolves out from verdigris the *sesquibasic acetate,* which presents itself on evaporating the solution, sometimes as an amorphous mass, and sometimes in crystalline grains of a pale blue colour. The sesquibasic acetate consists of 2 eq. of acetic acid, 3 eq. of oxide of copper, and 6 eq. of water; it loses 3 eq. of water at 212°. The *tribasic acetate* is the insoluble residue which remains after the lixiviation of verdigris. It is a clear green powder, which loses nothing at 212°. It contains 2 eq. of acetic acid, 6 eq. oxide of copper, and 3 eq. of water (Berzelius).

Acetate of copper also combines with acetate of lime, and with several other salts. The double *acetate and arsenite of copper* is a crystalline powder of a brilliant sea-green colour, which is used as a pigment, under the name of Schweinfurt green. It is obtained by mixing boiling solutions of equal parts of arsenious acid and neutral acetate of copper, adding to the mixture its own volume of cold water, and leaving the whole at rest for several days. It is a highly poisonous substance. From the analysis of Ehrmann, its formula is $C_4H_3CuO_4 + 3(CuO.AsO_3)$.

The most important *alloys of copper* are those which it forms with tin and zinc:

100 parts of copper with 5 tin (or 4 tin +1 zinc) form the bronze used for coin.

100 parts copper with 10 tin, form bronze and gun-metal.
100 parts copper with 20 to 25 tin, form bell-metal.
100 parts copper with 30 to 35 tin, form speculum-metal.

A little arsenic is generally added to the last alloy, to increase its whiteness.

The different varieties of brass are prepared, either by fusing together the two metals, copper and zinc, or by heating copper under a mixture of charcoal and calamine—an operation in which zinc is reduced and its vapour absorbed by the copper. Two or three parts of copper to one of zinc form common brass. The brass known as Muntz's white metal, which resists the solvent action of sea-water much better than pure copper, and is, in consequence largely used for the sheathing of ships, consists of 60 parts copper to 40 parts zinc, and appears to be the atomic compound Cu_2Zn. Equal parts of copper and zinc, or four of the former and one of the latter, give an alloy of a higher colour, resembling gold, and on that account called *similor*.

ESTIMATION OF COPPER, AND METHODS OF SEPARATING IT FROM OTHER METALS.

Copper is best precipitated by caustic potash, which when added to a boiling solution of a cupric salt, throws down the protoxide of copper in the form of a heavy black powder. From this precipitate every trace of potash may be removed by washing with hot water; and the washed precipitate may then be dried and ignited in a platinum or porcelain crucible. It must be weighed immediately after cooling, with the cover on the crucible, because it absorbs moisture rapidly from the air. It contains 79·82 per cent. of copper (H. Rose).

Copper is often precipitated from its solutions by hydrosulphuric acid. In that case the precipitated sulphide must be washed as quickly as possible with water containing hydrosulphuric acid, to prevent oxidation; the precipitate may then be dried, and the filter burnt with the precipitate on it, in a porcelain basin; after which the precipitate is treated with concentrated nitric acid, which dissolves it, with separation of sulphur, and the copper precipitated from the filtered solution by potash as above. The chief precaution to be attended to in this process is to wash the precipitated sulphide quickly, and to preserve it as completely as possible from contact with the air; otherwise the sulphide becomes partially oxidised and converted into sulphate, which being soluble, runs through the filter; when this takes place, the filtrate becomes brown, because the copper thus carried through, is again precipitated by hydrosulphuric acid.

Volumetric methods.—Copper may be volumetrically determined by means of a solution of permanganate of potash, by a process founded on that adopted by Margueritte for the determination of iron (p. 56.). The copper compound having been weighed and dissolved in acid, is mixed in a porcelain basin, with neutral tartrate of potash and excess of caustic potash, and then heated with a quantity of milk-sugar, or honey, sufficient to precipitate all the copper as cuprous oxide, the completion of the precipitation being indicated by the brown colour which the liquid then acquires. The precipitated cuprous oxide is then filtered, washed with hot water, and gently heated, together with the filter, with a mixture of pure sesquichloride of iron and dilute hydrochloric acid. It is thereby dissolved in the form of protochloride of copper, the sesquichloride of iron being at the same time reduced to protochloride:

$$Cu_2O + Fe_2Cl_3 + HCl = 2CuCl + 2FeCl + HO.$$

In the filtered liquid, diluted to a convenient strength and heated to about 86°, the quantity of iron in the state of protochloride is determined by a graduated solution of permanganate of potash in the manner already described (p. 56.), and thence the equivalent quantity of copper is readily determined. The presence of lead, zinc, bismuth, manganese, or iron, in the alkaline solution does not interfere with the process; silver or mercury must be separated before the precipitation of the cuprous oxide.

Another method, which appears to give very exact results, is to treat the copper-solution with iodide of potassium, whereby diniodide of copper is precipitated and iodine set free:

$$2(CuO.NO_5) + 2KI = Cu_2I + I + 2(KO.NO_5),$$

and remove the free iodine by means of a standard solution of hyposulphite of soda, whereby iodide of sodium and tetrathionate of soda are produced:

$$2(NaO.S_2O_2) + I = NaI + NaO.S_4O_5.$$

The copper-compound, if solid, an alloy for example, is dissolved in nitric acid; carbonate of soda added till a slight precipitate is formed; and this precipitate redissolved in acetic acid (free nitric acid would vitiate the result by decomposing the iodide of potassium). A quantity of iodide of potassium is next added, equal to at least six times the weight of the copper to be determined, and then the standard solution of hyposulphite of soda, in sufficient quantity to remove the greater part of the free iodine, which point will be indicated by the colour of the liquid changing from brown to yellow. Lastly, a clear solution of starch is added, and the addition of the hyposulphite of soda cautiously continued till the blue colour of the iodide of starch is completely destroyed. The solution of hyposulphite of soda is graduated by dissolving a known weight of pure electrotype copper in nitric acid, and proceeding as above. If the copper-compound contains a large quantity of lead or iron, these metals must be removed before commencing the determination, because the yellow colour of the iodide of lead and the red of the acetate of iron might interfere with the result (E. O. Brown).*

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* In a paper read before the Chemical Society, Nov. 17th, 1856, and to be Published in the 10th volume of the Society's Journal.

Pelouze's method, which consists in treating the copper solution with excess of ammonia, and precipitating the copper as oxysulphide, CuO.5CuS, by adding a graduated solution of sulphide of sodium till the blue colour is completely destroyed, appears, from Mr. Brown's experiments, to be liable to uncertainty from two causes: first, because the oxysulphide of copper reduces a portion of the protoxide of copper to dioxide, thereby rendering the solution colourless before the precipitation is complete; and secondly, because a portion of the sulphide of sodium is oxidised and converted into hyposulphite of soda.

Copper is separated from all the preceding metals, except cadmium, by means of hydrosulphuric acid, the solution being previously acidulated with hydrochloric or sulphuric acid. When zinc, nickel, or cobalt is present, a considerable excess of acid must be added, otherwise a portion of these metals will be precipitated together with the copper.

From *cadmium,* copper may be separated by carbonate of ammonia, which dissolves the copper and leaves the cadmium. The deposition of the cadmium is not complete till the liquid has been exposed for some time to the air. The separation is, however, better effected by adding to the solution of the two metals a quantity of cyanide of potassium, sufficient to redissolve the precipitate first formed, and then passing hydrosulphuric acid through the solution. Sulphide of cadium is then precipitated, and on driving off the excess of hydrosulphuric acid by heat, and adding more cyanide of potassium, the sulphide of copper remains completely dissolved. The copper may be precipitated as sulphide by mixing the filtrate with hydrochloric acid: but it is better to boil the filtrate with aqua-regia, till all the hydrocyanic acid is expelled, and then precipitate the copper by potash (Haidlen and Fresenius).

SECTION VIII.

LEAD.

Eq. 103·56 *or* 1294·5; Pb (*plumbum*).

Lead was one of the earliest known of the metals. A considerable number of its compounds are found in nature, but the sulphide, or galena, is the only one which is important as an ore of lead. The reduction of the metal is effected by heating the sulphide with exposure to air (or roasting), by which much of the sulphur is burned and escapes as sulphurous acid, and a fusible mixture of oxide of lead and sulphate of lead is produced. A fresh portion of the ore is added, which reacts upon the oxide of lead, the sulphur and oxygen forming sulphurous acid, and the lead of both oxide and sulphide being consequently reduced. Lime also is added, which decomposes the sulphate of lead, and exposes the oxide to be reduced by the fuel or by sulphide.

Lead has a bluish grey colour and strong metallic lustre, is very malleable, and so soft, when it has not been cooled rapidly, as to produce a metallic streak upon paper. Its density is 11·445, and is not increased by hammering. Its tenacity is less than that of any other ductile metal. The melting point of lead is 612°; on solidifying, this metal shrinks considerably, so that bullets cast in a mould are never quite round. Lead, like most other metals, assumes the octohedral form on crystallising. Lead is one of the less oxidable metals, at least when massive; its surface soon tarnishes, and is covered with a grey pellicle, which appears to defend the metal from further change. Rain or soft water cannot be preserved with safety in leaden cisterns, owing to the rapid formation of a white hydrated oxide at the line where the metal is exposed to both air and water; the oxide formed is soluble in pure water, and highly poisonous. But a small quantity of carbonic acid, which spring and well water usually contain, arrests the corrosion of the lead, by converting the oxide of lead into an insoluble salt, and prevents the contamination of the water.* Lead is not directly attacked by hydrochloric and sulphuric acids, at the usual temperature, but they favour its union with oxygen from the air. Its best solvent is nitric acid. Besides a protoxide, PbO, which is a powerful base, lead forms a suboxide Pb_2O, and a bioxide PbO_2, which do not combine with acids.

Suboxide of lead, Pb_2O, was discovered by Dulong, and is best obtained by heating the oxalate of lead to low redness in a small retort. It is dark grey, almost black, and pulverulent, and is not affected by metallic mercury. According to the analysis of Boussingault, it contains 1 eq. of oxygen to 2 eq. of lead. The grey pellicle which forms upon lead exposed to the air is, according to Berzelius, the same suboxide.

Protoxide of lead, PbO, 111·56 *or* 1394·5.—When a stream of air is thrown upon the surface of melted lead, the metal is rapidly converted into the protoxide, of a sulphur-yellow colour. The oxidated skimmings of the metal are, in this condition, termed *massicot*, and were at one time used as a yellow pigment. This preparation is fused at a bright red heat, and the oxide is thus separated from some metallic lead, with which it is intermixed in massicot. The fused oxide, on solidifying, forms a brick-red mass, which divides easily into crystalline scales, tough and not easily pulverised; they form *litharge*. The protoxide of lead can be obtained distinctly crystallised by various processes, but always presents itself in the same form, an octohedron with a rhombic base (Mitscherlich). By igniting the subnitrate of lead, the protoxide is obtained very pure, and of a rich lemon-yellow colour. Its density after fusion is 9·4214.

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* Dr. Christison's Treatise on Poisons.

When the acetate, or any other salt of lead, is precipitated by potash, the protoxide falls as a white hydrate, which may be dried at 212° without decomposition. It contains 3¾ per cent. water, and is, therefore, the hydrate $2PbO . HO$ (Mitscherlich). Oxide of lead likewise crystallises anhydrous, from solution, at the usual temperature, when precipitated under such circumstances that it cannot find water to combine with. This oxide dissolves in above 12,000 times its weight of distilled water, which acquires thereby an alkaline reaction, but not in water containing any saline matter. It is soluble in potash or soda; and the solutions, when evaporated, yield small crystals of an alkaline compound. A compound of lime and oxide of lead is obtained in needles, when hydrate of lime and that oxide are heated together, and the solution allowed to evaporate with exclusion of air. This solution has been employed to dye the hair black. Oxide of lead combines readily with the earths and metallic oxides by fusion, and when added to the materials of glass, imparts brilliancy to it and increased fusibility.

Oxide of lead is a powerful base, resembling baryta and strontia, and affords a class of salts which often agree in form and in general properties with the salts of these earths. Its carbonate occurs in *plumbocalcite*, in the form of carbonate of lime, an isomorphism by which the protoxide of lead is connected with the magnesian oxides. All its soluble salts are poisonous, although no salt of lead, with the exception of the insoluble carbonate, is highly so (Dr. A. T. Thomson). In a case of accidental poisoning by the carbonate, acetic acid proved a sufficient antidote.

Caustic alkalies precipitate lead from its solutions as a white hydrate, soluble in potash and soda, insoluble in ammonia. *Alkaline carbonates* throw down a white precipitate of carbonate of lead, insoluble in excess of the reagent. *Hydrochloric acid* and *soluble chlorides* produce in moderately strong lead-solutions, a white crystalline precipitate of chloride of lead, easily soluble in potash, insoluble in ammonia, soluble in a considerable quantity of water; in dilute solutions (*e. g.* in a solution of 1 part of nitrate of lead in 100 parts of water) no precipitate is formed. *Sulphuric acid* and *soluble sulphates* throw down, even from very dilute solutions, a white, pulverulent precipitate of sulphate of lead, easily soluble in potash, soluble also, though slowly, in hydrochloric and nitric acid; but by adding a considerable excess of sulphuric acid, lead may be completely precipitated even from solutions containing hydrochloric or nitric acid. According to Lassaigne, 1 part of oxide of lead (in the form of nitrate) dissolved in 25,000 parts of water, gives an opalescence with sulphate of soda, after a quarter of an hour. *Hydrosulphuric acid* and *alkaline sulphides* produce a black precipitate of sulphide of lead, insoluble in sulphide of ammonium. In very dilute solutions, cnly a brown colouring is produced, the limit of the reaction being attained, according to Lassaigne, with 1 part of oxide of lead (in the form of nitrate) dissolved in 350,000 parts of water. If the solution of the lead-salt contains free hydrochloric acid, the precipitate is red or yellow, and a large excess of hydrochloric acid prevents it altogether. *Iodide of potassium* produces a bright yellow precipitate of iodide of lead, which dissolves in boiling water and separates again on cooling in crystalline spangles, exhibiting a beautiful play of colours. *Chromate* and *bichromate of potash* throw down yellow chromate of lead, easily soluble in caustic potash. The limit of this reaction is attained with 1 part of oxide of lead (in the form of nitrate) dissolved in 70,000 parts of water (Harting). *Iron* and *zinc* throw down metallic lead. If a mass of zinc be suspended in a solution, made by dissolving one ounce of acetate of lead in two pounds of distilled water, the lead is precipitated in beautiful crystalline plates, which are deposited not only in metallic contact with the zinc, but extend from it to a considerable distance in the liquid, forming what is called the lead-tree. Lead-salts, mixed with carbonate of soda or cyanide of potassium, and ignited on charcoal before the blow-pipe, yield a malleable button of lead. The oxides of lead are reduced by simply heating them with the blowpipe flame on charcoal.

Sesquioxide of lead, Pb_2O_3.—Hypochlorite of soda throws down from lead-salts a reddish-yellow mixture of sesquioxide and chloride of lead. The sesquioxide may be obtained free from chloride by supersaturating a solution of nitrate of lead with potash, in quantity sufficient to redissolve the precipitated hydrate, and then treating it with hypochlorite of soda. The sesquioxide is converted by acids into bioxide and an ordinary salt of lead (Winkelblech).

Bioxide or peroxide of lead, PbO_2, may be obtained in the same manner as the peroxides of cobalt and nickel, by exposing the protoxide suspended in water to a stream of chlorine; also by fusing protoxide of lead with chlorate of potash at a temperature short of redness; or by digesting the following intermediate oxide, minium, in diluted nitric acid, which dissolves the protoxide of lead, decanting off the nitrate of lead, and washing the powder which remains with boiling water. Wöhler precipitates a solution of 4 parts of acetate of lead with a solution of 3 parts or rather more of crystallised carbonate of soda, and passes chlorine gas through the resulting thin pulpy mass, till the whole of the carbonate of lead is converted into brown bioxide, amounting to 2½ parts, which may then be washed. No chloride of lead is formed in this reaction, the whole of the chlorine combining with the sodium, while acetic and carbonic acid are set free. Bioxide of lead is of a dark earthy-brown colour. It loses half its oxygen by ignition; absorbs sulphurous acid with great avidity, and becomes sulphate of lead; and affords chlorine when digested in hydrochloric acid.

Minium or red lead is formed by heating massicot or protoxide of lead, which has not been fused, to incipient redness in a flat furnace, of a particular construction, and directing a current of air upon its surface. Oxygen is absorbed, and an oxide formed of a fine red colour, with a shade of yellow. It is not constant in composition. The proportion of oxygen, when the absorption is least considerable, approaches that of a compound containing $3PbO.PbO_2$; and such was the composition of a crystallised compound of a fine red colour, formed by accident in a minium furnace, and analysed by Houton-Labillardière. But when the absorption is favoured by time and most considerable, it approaches but never exceeds 2·4 per cent. of the original weight of the protoxide. This result agrees with the formula Pb_3O_4, and accordingly minium may be regarded as a compound of protoxide and bioxide of lead $2PbO.PbO_2$, or of protoxide and sesquioxide $PbO.Pb_2O_3$. A sample of minium analysed by Longchamps contained $5PbO.PbO_2$. The finest minium is obtained by calcining oxide of lead from the carbonate, at about 600°.

Minium is not altered by being heated in a solution of acetate of lead, which is capable of dissolving free protoxide of lead. When heated to redness, it loses oxygen, and leaves the protoxide. It does not combine with acids, but is resolved by a strong acid into bioxide of lead and protoxide, the latter combining with the acid. When minium is treated with concentrated acetic acid, it first becomes white, and then dissolves entirely in a new quantity of acid without colouring it. But the solution gradually decomposes, and bioxide of lead separates from it of a blackish-brown colour (Berzelius).

Protosulphide of lead, PbS, is thrown down from salts of lead, by hydrosulphuric acid, as a black precipitate, which is insoluble in diluted acids or in alkalies. It forms also the ore galena, which crystallises in the cube and other forms of the regular system; its density is 7·585. Sulphide of lead is decomposed easily by nitric acid, and converted into nitrate and sulphate of lead, with separation of a little sulphur. The more concentrated the nitric acid, the greater is the quantity of sulphate produced Recently precipitated sulphide of lead may be completely dissolved in the form of nitrate by boiling with dilute nitric acid. Concentrated and boiling hydrochloric acid dissolves sulphide of lead, with disengagement of hydrosulphuric acid gas. Galena may be united by fusion with more lead, and gives the subsulphides Pb_4S, and Pb_2S. When a solution of persulphide of potassium is added to a salt of lead, a blood-red precipitate appears, which is a persulphide of lead, but is almost immediately changed into the black protosulphide of lead and free sulphur.

Chloride of lead, PbCl, 139·06 *or* 1738·25.—Lead dissolves slowly in hydrochloric acid, by substitution for hydrogen, forming the chloride of lead, but only when assisted by the action of the air. The same compound is obtained by digesting oxide of lead in hydrochloric acid, and also falls as a white precipitate, when a salt of lead is added to any soluble chloride. The chloride of lead is soluble in 135 times its weight of cold water, and more so in hot water, from which it crystallises on cooling in long flattened acicular crystals, which are anhydrous. It is very fusible, and may be sublimed at a higher temperature

Oxychloride of lead. — Chloride of lead combines in five different proportions with the protoxide, forming the following compounds: — *a.* 3PbCl.PbO. Four parts of chloride of lead ignited with 1 part of litharge yield a fused, laminar, pearl-grey mixture, which, when triturated with water, swells up to a bulky mass having the above composition (Vauquelin). The same substance is obtained by Mr. Pattinson, by decomposing carbonate of lead with lime-water, and used as a white pigment.—*b.* PbCl.PbO. Formed by igniting chloride of lead in contact with air till it no longer fumes, or by fusing chloride and carbonate of lead together. Carbonic acid is then set free, and a compound formed which is of a deep yellow colour while fused, but as it cools assumes a lemon-yellow colour, and becomes nacreous and crystalline (Döbereiner).—*c.* PbCl.2PbO. This compound forms the mineral *Mendipite*, found at Mendip, in Somersetshire, where it occurs in yellowish-white, right rhombic prisms, which are harder than gypsum, translucent, and have an adamantine lustre (Berzelius). It also occurs, and in a state of greater purity, at Brilon, near Stadtbergen, in Westphalia; the crystals there found are white, translucent, and have a mother-of-pearl lustre on the cleavage surfaces.* — *d.* $PbCl.3PbO$. Obtained by fusing 1 eq. chloride of lead with 3 eq. of the protoxide; also in the hydrated state, $PbCl.3PbO + HO$ or $4PbO.HCl$, by decomposing chloride of lead with ammonia; by precipitating subacetate of lead with common salt; and by decomposing a solution of common salt with protoxide of lead. The hydrate is a white flocculent mass, and when fused yields the anhydrous compound, which is a greenish-yellow laminated mass, forming a yellow powder. — *e.* $PbCl.5PbO$. Obtained by fusing 1 eq. chloride of lead with 5 eq. of the protoxide. Orange-yellow substance, yielding a deep yellow powder. — *f.* $PbCl.7PbO$, is produced on fusing by heat a mixture of 10 parts of pure oxide of lead and 1 part of pure sal-ammoniac, a portion of the lead being at the same time reduced. The surbasic chloride when fused affords cubic crystals on cooling slowly. It forms in that state a beautiful yellow pigment, known as Turner's yellow in this country, and Cassel yellow in Germany. It was prepared in England by digesting litharge with half its weight of common salt, a portion of which is converted into caustic soda, and afterwards washing and fusing the oxychloride formed. But it is sufficient to use 1 part of salt to 7 parts of oxide of lead in this decomposition.

Bichloride of lead, $PbCl_2$.—Bioxide of lead dissolves, without evolution of gas, in cold dilute hydrochloric acid, forming a rose-coloured liquid, from which alkalies throw down the bioxide in its original state. The rose-coloured acid solution, evaporated in vacuo over strong potash-ley, yields crystals of chloride of lead PbCl, togther with crystals of a different character, which appear to consist of $PbCl_2$ (Rivot, Beudant, and Daguin).

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* Rhodius, Ann. Ch. Pharm. lxii. 373.

Bromide of lead, PbBr, is much less soluble in water than the chloride; hence, in a liquid containing hydrochloric and hydrobromic acids, if the bromine be precipitated by acetate of lead, the filtered liquid will still contain chlorine, which may then be detected by adding nitrate of silver (H. Rose).

Iodide of lead, PbI, 229·92 *or* 2874.—Appears as a beautiful lemon-yellow powder, when iodide of potassium is added to a salt of lead. It is soluble in 194 parts of boiling water, and in 1235 parts of water at the usual temperature, and may be obtained from solution in brilliant hexagonal scales of a golden-yellow colour. A compound of a paler yellow, which appears in dilute solutions and when the salt of lead is in excess, is a basic iodide. M. Denot finds three oxy-iodides of lead, containing 1 eq. of iodide of lead to 1 eq., 2 eq., and 5 eq. of oxide of lead, and always 1 eq. of water, which last they do not lose below a temperature of about 400°.

Neutral iodide of lead, PbI, is decomposed by metallic chlorides, yielding, when the iodide is in excess, compounds which may be regarded as iodide of lead, in which part of the iodine is replaced by chlorine. Sesquichloride of iron and protochloride of copper separate free iodine (A. Engelhardt).

Cyanide of lead, PbCy, is a white insoluble powder, obtained by precipitation.

Carbonate of lead, ceruse, white lead; $PbO.CO_2$; 133·56 *or* 1669·5. — Occurs in nature well crystallised, in the form of carbonate of baryta. It is precipitated as a white powder, of which the grains, although very minute, are crystalline, when an alkaline carbonate is added to the acetate or nitrate of lead. The precipitate is anhydrous. When oxide of lead is left covered with water in an open vessel, it absorbs carbonic acid, and becomes white, forming the subcarbonate $PbO.CO_2 + PbO.HO$.

Carbonate of lead is invaluable as a white pigment, from its great opacity, which gives it that property called *body* by painters, and enables it to cover well. As precipitated by an alkaline carbonate, it is deficient in body, owing to the transparency of the crystalline grains composing the precipitate. It is also a neutral carbonate, as thus prepared, and differs in composition from the ceruse of commerce, which Mulder finds always to contain hydrated oxide of lead in combination with the carbonate of lead. The result of Mulder's analyses of numerous specimens of white lead, is, that there are three varieties of that substance, the composition of which is expressed by the three following formulæ:—

$$2(PbO.CO_2)+PbO.HO;$$
$$5(PbO.CO_2)+3(PbO.HO); \text{ and}$$
$$3(PbO.CO_2)+PbO.HO.$$

Mr. J. A. Phillips has also examined several specimens of white lead prepared by the Dutch process. Four samples gave by analysis the formula, $2(PbO.CO_2)+PbO.HO$; one gave $3(PbO.CO_2)+PbO.HO$; another, $5(PbO.CO_2)+PbO.HO$.* Dr. T. Richardson also found that varieties of white lead contain a portion of oxide of lead, in addition to the carbonate, and so far confirms the conclusions of Mulder.

In the old or Dutch mode of preparing white lead, which is still extensively practised, thin sheets of the metal are placed over gallipots containing weak acetic acid (water with about 2½ per cent. dry acid), themselves imbedded in fermenting tan, the temperature of which varies from 140° to 150°. The action is often very rapid, and the metal disappears in a few weeks to the centre of the sheet. In this process, from 2 to 2½ tons of lead (4480 to 5600 pounds) are converted into carbonate, by a quantity of vinegar which does not contain more than the small quantity of 50 pounds of dry acetic acid. Hence the metal is certainly neither oxidised nor carbonated in this process, at the expense of the acetic acid. The oxygen must be derived from the air, and the carbonic acid from the fermenting tan. In the newer process, litharge, without any preparation, is mixed with water and about 1 per cent. of acetate of lead, and carbonic acid gas passed over it; the oxide of lead is rapidly converted into excellent ceruse. There can be little doubt that all the oxide of lead is successively dissolved by the acetate, and presented to the carbonic acid as a soluble subacetate; a compound which, it is known, absorbs carbonic acid with the greatest avidity, and allows its excess of oxide to precipitate as carbonate of lead. The new process supplies likewise the theory of the old one, the function of the acetic acid being manifestly the same in both processes. Nitrate of lead has been substituted for the acetate, with other things the same as in the last process.

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* Chem. Soc. Qu Pt. iv. p. 165.

Sulphate of lead; PbO, SO_3; 151·56 *or* 1894·5.—This salt is precipitated when sulphuric acid or a soluble sulphate is added to a solution of acetate or nitrate of lead, as a white, dense, insoluble precipitate, which appears by the microscope to be composed of minute crystals. It is also formed by the action of strong nitric acid on sulphide of lead. Sulphate of lead contains in 100 parts, 26·44 sulphuric acid and 73·56 oxide of lead, and may be exposed to a red heat without decomposition. Dr. Richardson finds that this salt acquires considerable opacity, and may be substituted for ceruse, when prepared in a mode analogous to the new process for that substance; namely, by supplying sulphuric acid, in a gradual manner, to a thick mixture of litharge and water containing a small proportion of acetate of lead. In this manner the sulphate of lead may be obtained united with any desirable excess of oxide of lead.

Nitrate of lead; $PbO.NO_5$; 165·56 *or* 2069·5.— Obtained by dissolving litharge, at the boiling point, in slightly diluted nitric acid, which should be free from hydrochloric and sulphuric acids. The neutral nitrate crystallises in large octohedrons, with the secondary faces of the cube, sometimes transparent, although generally white and opaque. The crystals are anhydrous; they are soluble in 7½ times their weight ot cold, and in a much smaller quantity of hot water. Nitrate of lead is decomposed by an incipient red heat, yielding a mixture of oxygen gas and peroxide of nitrogen (which is prepared in this way), and leaving the yellow oxide of lead. When a small quantity of ammonia is added to nitrate of lead, or when a dilute solution of the neutral salt is boiled with oxide of lead in fine powder, a soluble *bibasic nitrate of lead* is formed $PbO.NO_5+PbO$. It crystallises during evaporation in fine scales, or in little opaque grains, which are anhydrous. The granular crystals decrepitate when heated, with extraordinary force. The *tribasic nitrate of lead* precipitates when ammonia is added in very slight excess to a solution of nitrate of lead. Its constituents are $2(3PbO.NO_5)+3HO$ (Berzelius). It is a white powder, which is soluble to a small extent in pure water. When nitrate of lead is digested with a considerable excess of ammonia, the decomposition stops at the point at which 6 eq. of oxide of lead are combined with 1 eq. of nitric acid. The *sexbasic nitrate of lead* contains $2(6PbO.NO_5)+3HO$ (Berzelius).

Nitrites of lead. — When a solution of 100 parts of nitrate of lead is boiled with 78 parts of metallic lead in thin turnings, the lead is dissolved, and a little nitric oxide is evolved, in consequence of a partial decomposition of nitrous acid previously formed. The solution is alkaline and yellow; and gives, on cooling, brilliant crystalline plates of a golden yellow colour, which consist of the *bibasic nitrite of lead*, $2PbO.NO_3$. By dissolving 100 parts of this salt in water at 167° (75° C.), and then mixing with the solution 35 parts of oil of vitriol, previously diluted with four times its weight of water, one half of the oxide of lead is precipitated as sulphate of lead, and a solution is obtained of a deep yellow colour, from which the *neutral nitrite of lead*, $PbO.NO_3+HO$, crystallises. This salt gives yellow crystals, resembling the nitrate in form. Its solution absorbs oxygen from the air, and, like all the nitrites, gives off nitric oxide at 176° (80° C.), while a subnitrite of lead precipitates. Berzelius, to whom we are indebted for the preceding facts, also formed a *quadribasic nitrite of lead*, containing $NO_3.4PbO + HO$, by boiling 1 part of nitrate of lead, and 1½ parts or more of metallic lead, in a long-necked flask for 12 hours, then filtering and leaving the solution to crystallise by cooling: it thus yields pale, flesh-coloured, silky needles, or, if rapidly cooled, a white powder.

The nitrites of lead have also been examined by other chemists, who have obtained results differing from those of Berzelius. Thus, Péligot and others found that Berzelius's bibasic nitrite contains the elements of 2 eq. of oxide of lead, 1 eq. of hyponitric acid, NO_4, and 1 eq. of water. Gerhardt therefore regards it as a compound of bibasic nitrate and bibasic nitrite of lead:—

$$2(PbO.NO_4) = 2PbO.NO_3 + 2PbO.NO_5.$$

and expresses its formation by the equation:—

$$2(PbO.NO_5) + 2Pb = 2PbO.NO_5 + 2PbO.NO_3.$$

If the action of the metallic lead be further continued, a fresh portion of nitrate is deoxidised, and the result is an orange-coloured salt, containing $7PbO.2NO_4$ (Péligot), which Gerhardt regards as a double salt more basic than the former:

$$7PbO.2NO_4 = 4PbO.NO_3 + 3PbO.NO_5.$$

Finally, by the continued action of the lead, the subnitrate contained in these two salts is likewise reduced, and a subnitrite is formed, viz., either Berzelius's quadrobasic salt, $4PbO.NO_3$, or a bibasic nitrite $2PbO.NO_3$, obtained by Bromeis. The last salt crystallises in long golden-yellow needles containing 1 eq. of water.*

Phosphate of lead.—On mixing nitrate of lead with ordinary phosphate of soda, a precipitate is formed containing the two salts $3PbO.PO_5$ and $2PbO.HO.PO_5$. The latter is obtained pure by precipitating a boiling solution of nitrate of lead with pure phosphoric acid. This salt dissolves in nitric acid and fixed alkalies, but very sparingly in acetic acid; ammonia converts it into $3PbO.PO_5$. It fuses readily before the blowpipe, and crystallises on cooling in well defined polyhedrons. When strongly ignited with charcoal, it gives off phosphorus and carbonic oxide, and leaves metallic lead.

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* For a more detailed account of the nitrates and nitrites of lead, see Gmelin's Handbook, Translation, v. 152—157.

Chlorite of lead, $PbO.ClO_3$, is obtained in sulphur-yellow crystalline scales by precipitating nitrate of lead with an excess of chlorite of baryta containing free chlorous acid. It decomposes at 259° with a kind of explosion, and sets fire to flowers of sulphur triturated with it. Sulphuric acid diluted with an equal weight of water, decomposes it, especially between 104° and 122°, evolving pure chlorous acid gas, and leaving 88·75 per cent. of sulphate of lead (Millon).

Chlorate of lead, $PbO.ClO_5 + HO$, is obtained by cooling a hot solution of oxide of lead in aqueous chloric acid, in rhomboïdal prisms belonging to the oblique prismatic system, and isomorphous with the analogously constituted crystals of chlorate of baryta. These crystals, when heated, leave the yellow oxychloride $PbO.2PbCl$ (Vauquelin, Wächter, Vogel).

Perchlorate of lead, $PbO.ClO_7$.—The solution of oxide of lead in warm aqueous perchloric acid, yields small prisms having a sweet but highly astringent taste, soluble in their own weight of water, but not deliquescent (Serullas). By boiling a concentrated solution of this salt with carbonate of lead, a solution of a basic salt is obtained, which if the excess of base is very large, yields by evaporation, dull, indistinct crystals, which are resolved by water into a solution of bibasic salt, and a white insoluble residue. When the excess of base is less, or when the solution of the bibasic salt is left to evaporate, crystals of two different forms are obtained; both, however, containing $2PbO.ClO_7 + 2HO$ (Marignac).

Chlorophosphate of lead, $PbCl + 3(3PbO.PO_5)$, occurs as *pyromorphite* and *green* and *brown lead-ore*. The crystals belong to the hexagonal system, and have the hardness of apatite. It fuses readily, and on cooling solidifies with vivid incandescence into an angular crystalline mass. In some of these ores, the chloride of lead is partly replaced by fluoride of calcium, and the triphosphate of lead by the triphosphate of calcium or trisarseniate of lead. The calcareous ores may be regarded as mixtures of apatite and pyromorphite. The same compound containing, however, an atom of water, is formed artificially on pouring a boiling solution of chloride of lead into a boiling solution of phosphate of soda, the latter being in excess (Heintz). When, on the contrary, a boiling solution of phosphate of soda is poured into an excess of chloride of lead, a precipitate is formed, which, according to Heintz, is $2(3PbO.PO_5) + PbCl$, but, according to Gerhardt, $2PbO.HO.PO_5 + PbCl$.

Acetate of lead, $PbO.(C_4H_3O_3) + 3HO$.—This salt is met with well crystallised, and in a state of great purity, in commerce. It is generally prepared by dissolving litharge in the acetic acid procured by the distillation of wood. It crystallises in flattened four-sided prisms; has a taste which is first sweet and then astringent; is very soluble in water, 100 parts of water dissolving 59 of the salt at 60°; and dissolves in 8 parts of alcohol. It effloresces in air, and is apt to be partially decomposed by the carbonic acid of the air, and thus to become partially insoluble. It loses the whole of its water when dried at the usual temperature in vacuo. M. Payen crystallised the anhydrous acetate from solution in absolute alcohol.

Tribasic subacetate of lead, $PbO.(C_4H_3O_3) + 2PbO$, is formed by digesting oxide of lead in a solution of the neutral salt, till it is strongly alkaline. This salt does not crystallise when so prepared, but may be dried, and then contains no water. It is very soluble, but must be dissolved in distilled water, as the carbonic, hydrochloric and other acids in well water precipitate its oxide of lead. M. Payen has observed that the tribasic subacetate crystallises readily, in fine prismatic needles, when formed by adding ammonia to a moderately strong solution of the neutral acetate. The crystals contain 1 eq. of water, which they lose at 212°. The acetate of ammonia, formed at the same time, appears to give stability to the subacetate of lead in solution, and prevents an excess of a whole equivalent of ammonia from throwing down any oxide of lead from the solution. This ammoniacal solution of the subacetate of lead, prepared without an excess of ammonia, is a convenient form in which to apply that salt as a reagent.*

Sesquibasic acetate of lead, $3PbO.2(C_4H_3O_3)+HO$.—This salt was obtained by Payen by adding 1 eq. of the neutral acetate to a concentrated and boiling solution of 1 eq. of the tribasic acetate. It is also produced when the neutral and anhydrous acetate of lead is heated in a retort or porcelain capsule, till the whole, after being liquid, becomes a white and porous mass. The sesquibasic acetate is then formed by the decomposition of 3 eq. of neutral acetate of lead, from which there separate the elements of 1 eq. of acetic acid, in the form of carbonic acid and acetone (Matteucci and Wöhler). This basic salt is very soluble, and crystallises in plates of a pearly lustre. Another method of obtaining it is to digest an aqueous solution of 2 eq. of the neutral acetate with 1 eq. of protoxide of lead free from carbonate, till it dissolves, and evaporate the filtrate in vacuo over oil of vitriol.

A *sexbasic acetate of lead*, $6PbO.(C_4H_3O_3)$, is formed on dropping a solution of the neutral, or of tribasic acetate of lead, into excess of ammonia. It is a white precipitate, which when examined by the microscope, has a crystalline aspect. It contains a little water, which it loses when dried in vacuo.

A *bibasic acetate*, $2PbO.(C_4H_3O_3)$, is also formed, according to Döbereiner and Schindler, by boiling 1 eq. of neutral acetate of lead with 1 eq. of the protoxide.

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* Mémoire sur les Acétates et le Protoxide de Plomb, par M. Payen, An. de Chim. et de Phys. t. lxvi. p. 37.

The common *extractum Saturni* of the pharmacopœias appears to consist chiefly of bibasic acetate, containing more or less of the tribasic and sesquibasic salts.

Alloys of lead.—Lead and tin may be fused together in all proportions. M. Rudberg finds that these metals combine in certain definite proportions, having fixed points of congelation:—

1 atom of lead and 3 atoms of tin, congeal at 368·6°.
1 atom of lead and 1 atom of tin, at 464°.
2 atoms of lead and 1 atom of tin, at 518°.
3 atoms of lead and 1 atom of tin, at 536°.

A thermometer placed in a fluid alloy of 1 atom of lead and 2 atoms of tin, becomes stationary when the temperature falls to 392°; a portion then solidifies, and a more fusible alloy separates; the temperature again falls, and afterwards becomes stationary at 368·6°, the crystallising point of the alloy composed of 1 atom of lead and 3 atoms of tin. If the alloy contains so much tin that its point of complete congelation is below 368·6°, the last compound always separates from it at that point, and the thermometer remains stationary for a time, whatever may be the proportion of the metals in the alloy.* *Fine solder* is an alloy of 2 parts of tin and 1 of lead; it fuses at about 360°, and is much employed in tinning copper. *Coarse solder* contains one fourth of tin, and fuses at about 500°; it is the substance employed for soldering by plumbers.

Lead, as reduced from the native sulphide, always contains a little silver. The latter is separated by allowing two or three tons of the melted metal to cool slowly in a hemispherical iron pot, when the lead, as it solidifies, separates in crystals, which can be raked out. The silver remains almost wholly in the more fusible portion, or what may be looked upon as the mother-liquor of these crystals; so that by this operation the argentiferous alloy is greatly concentrated. This mode of separation was discovered by Mr. Pattinson of Newcastle. To separate the remaining lead, much of it is converted into massicot, by the action of air upon its surface, in the shallow furnace used for that preparation; and the last portions of lead are removed by continuing the oxidation upon a porous bason or *cupel* of bone-earth, which imbibes the fused oxide of lead, while the melted silver is found in a state of purity upon the surface of the cupel, not being oxidable at a high temperature.

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* Rudberg, An. Ch. Phys. [2.] xlviii. 363.

ESTIMATION OF LEAD, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Lead may be estimated either as protoxide or as sulphate. For the former mode of estimation, it is best to precipitate by oxalate of ammonia, the solution being neutral or rendered very slightly alkaline by ammonia. The oxalate of lead, after being washed and dried, is then to be ignited in an open porcelain crucible, whereby it is converted into protoxide. As lead is very easily reduced by carbonaceous matter at a red heat, the precipitate must not be ignited in contact with the filter; but the filter, after the greater part of the precipitate has been removed from it, must be held on the point of a fine platinum wire above the crucible, and set on fire, so that the ashes may drop in; the precipitate may then be added, and the ignition completed. The protoxide contains 92·83 per cent. of metallic lead. Lead may also be precipitated by carbonate of ammonia, to which a little free ammonia has been added, and the carbonate of lead treated as above.

In precipitating lead as sulphate, if the solution be neutral, the precipitation is best effected by sulphate of soda; the sulphate of lead may then be washed on a filter, dried and ignited; but if the solution contains free nitric acid, it is best to precipitate by excess of sulphuric acid, then evaporate to dryness, and ignite till all excess of acid is driven off; treat the residue with water to dissolve out any soluble salts that may be present; wash the sulphate of lead on a filter, and then dry and ignite it, burning the filter separately as above. The sulphate contains 68·32 per cent. of lead.

From the *alkalies* and *earths*, and from *manganese*, *iron*, *cobalt*, *nickel*, and *zinc*, lead is easily separated by hydrosulphuric acid, the solution being previously acidulated with nitric acid. The precipitated sulphide is washed and dried, then placed, together with the filter (which should be as small as possible), in a porcelain dish, covered over with a glass plate or a funnel, and treated with fuming nitric acid, added cautiously and by small portions at a time. Violent action takes place, and the sulphide of lead is converted into sulphate. A portion may, however, be converted into nitrate, with separation of sulphur: hence, to insure complete conversion into sulphate, it is necessary to add a few drops of strong sulphuric acid. The product must then be strongly ignited to drive off the excess of sulphuric acid, and burn away the remaining organic matter of the filter.

From *cadmium* and *copper*, lead is easily separated by sulphuric acid.

ORDER V.

OTHER METALS PROPER HAVING ISOMORPHOUS RELATIONS WITH THE MAGNESIAN FAMILY.

SECTION I.

TIN.

Eq. 58·82 *or* 735·25; Sn (*stannum*).

TIN does not occur native, but its common ore is reduced by a simple process, and mankind appear to have been in possession of this metal from the earliest ages. The most productive mines of tin are those of Cornwall, from which the ancients appear to have derived their principal supply of this metal, and those of the peninsula of Malacca and island of Banca in India.

The only important ore of tin is the bioxide, which is found in Cornwall, both in veins traversing the primary rocks, and in alluvial deposits in their neighbourhood. In the latter case, the ore presents itself in rounded grains of greater or less size, which form together a bed covered by clay and gravel. This ore has evidently been removed from its original situation, and the grains rounded by the action of water, which has at the same time divested it of the other metallic ores with which it is accompanied in the vein; these being softer are more easily reduced to powder, and have been carried away by the stream. This ore, called *stream tin,* is easily reduced by coal, and gives the purest tin. The metal from the ore of the veins is contaminated with iron, copper, arsenic, and antimony, from which a portion of it is partially purified by *liquation.* Bars of the impure metal are exposed to a moderate heat, by which the pure tin is first melted, and separates it from a less fusible alloy containing the foreign metals. The purer portion is called *grain tin,* and the other, *ordinary tin* or *block tin.* The mass of grain tin is heated till it becomes brittle, and then let fall from a height. By this it splits into irregular prisms, somewhat resembling basaltic columns. This splitting is a mark of the purity of the tin, for it does not happen when the tin is contaminated by other metals.

Pure tin is white, with a bluish tinge, very soft, and so malleable, that it may be beaten into thin leaves, tinfoil not being more than 1-1000th of an inch in thickness. When a bar of tin is bent, it emits a grating sound, which is characteristic; and when bent backwards and forwards rapidly, several times in succession, becomes so hot that it cannot be held in the hand. At the temperature of boiling water, tin can be drawn out into wire, which is very soft and flexible, but deficient in tenacity. The density of pure tin is 7·285, or 7·293 after being laminated; that of the tin of commerce is said to vary from 7·56 to 7·6. Its point of fusion is 442°, according to Crichton and Rudberg; 4456°, according to Kupffer. Tin is volatile at a very high temperature. The brilliancy of the surface of tin is but slowly impaired by exposure to air, and even in water it is scarcely acted upon. Hence the great value of this metal for culinary vessels, and for covering the more oxidable metals, such as iron and copper, when employed as such. Three oxides of tin are known, the protoxide SnO, sesquioxide Sn_2O_3, and bioxide SnO_2.

Protoxide of tin, Stannous oxide; SnO, 66·82 *or* 835·25. Tin dissolves in undiluted hydrochloric acid, at the boiling temperature, by substitution for hydrogen, and forms the protochloride of tin. From this the protoxide is precipitated by an alkaline carbonate, as a white hydrate, which may be washed with tepid water and dried at a temperature not exceeding 176°. It does not contain a trace of carbonic acid.

This white powder dried more strongly in a retort filled with carbonic acid, and heated to redness, gives the anhydrous oxide as a black powder, the density of which is 6·666. In this state, the oxide is permanent; but if a body at a red heat is brought in contact with it in open air, it takes fire and burns, and is entirely converted into bioxide. If hydrated stannous oxide be boiled with a quantity of potash not sufficient to dissolve it entirely, the undissolved portion is converted into small, hard, shining, black crystals of anhydrous stannous oxide, which, when heated to 392°, decrepitate, swell up, fall to pieces, and are converted into an olive-green powder, consisting also of the anhydrous protoxide. Again, on evaporating a very dilute solution of sal-ammoniac, in which hydrated stannous oxide is diffused, that compound is converted, as soon as the sal-ammoniac crystallises, into anhydrous stannous oxide, having the form of a cinnabar-coloured powder. There are, therefore, three modifications of stannous oxide, black, olive-green, and red (Fremy). The red modification is also obtained by digesting thoroughly washed hydrated stannous oxide at a temperature of 133°, in a slightly acid solution of stannous acetate, having a density of 1·06 (Roth).

Protoxide of tin dissolves in acids, and with more facility when hydrated than after being ignited. This oxide is also dissolved by potash and soda, but the solution after a time undergoes decomposition; metallic tin is deposited, and the bioxide is found in solution. The solution of a stannous salt, and of a stannic salt also, is apt to undergo decomposition, when largely diluted with water, and to deposit a subsalt. Stannous salts absorb oxygen from the air, and have a great affinity for that element; they convert the sesquioxide of iron into protoxide, and throw down mercury, silver and platinum in the metallic state from their solutions. *Chloride of gold* produces a purple precipitate in a stannous salt, consisting, it is believed, of the bioxide of tin in combination with protoxide of gold, a test by which the protoxide of tin may always be distinguished. *Hydrosulphuric acid* produces in neutral or acid solutions of stannous salts, a brown-black precipitate of protosulphide of tin, which, when gently heated with a considerable quantity of sulphide of ammonium containing excess of sulphur, is converted into the bisulphide and dissolved; acids added in excess to this solution precipitate the yellow bisulphide. *Caustic alkalies* and *alkaline carbonates*, added to stannous salts, throw down a white precipitate of hydrated stannous oxide, soluble in caustic potash or soda, but not in ammonia. *Ferrocyanide of potassium* produces a white precipitate, soluble in hydrochloric acid.

Protosulphide of tin, SnS, is formed when sulphur is mixed with tin heated above its melting point; it is also obtained in small dark grey crystalline laminæ, of sp. gr. 4·973, by adding the hydrated sulphide precipitated from a stannous salt by hydrosulphuric acid, to anhydrous protochloride of tin in the melted state, and removing the excess of the protochloride with dilute hydrochloric acid. It is decomposed by dilute hydrochloric acid, with evolution of hydrosulphuric acid.

Protochloride of tin, Salt of tin; $SnCl$.—This salt may be obtained in the anhydrous state by gradually heating a mixture of equal weights of calomel and tin, and finally distilling the protochloride at a strong red heat. The fused mass on cooling forms a grey solid, of considerable lustre, and having a vitreous fracture. The hydrated chloride, known in commerce as salt of tin, is procured by evaporating the solution of tin in concentrated hydrochloric acid to the point of crystallisation. It is thus obtained in needles, or in larger four-sided prismatic crystals containing 2 eq. of water. They fuse between 100° and 105°. The specific gravity of the crystals is 2·710 at 60°; that of the fused mass at 100°, is 2·588 (Penny). The salt parts with the greater portion, if not the whole of its water at 212°, but if distilled at a higher temperature, loses hydrochloric acid also, and leaves an oxychloride of tin. It dissolves completely in a small quantity of water; but when treated with a large quantity, is partly decomposed, hydrochloric acid being dissolved, and a light milk-white powder separating, which is a basic chloride, or oxychloride, $SnCl.SnO + 2HO$. Both the crystals and the solution absorb oxygen from the air, and then a basic salt of the sesquioxide is formed which is also insoluble in water. From both these causes, a complete and clear solution of the salt of tin is rarely obtained, unless the water is previously acidulated with hydrochloric acid. This salt is entirely soluble in caustic alkali, but the solution is liable to an ulterior change already mentioned. One part of crystallised protochloride of tin dissolved, together with 3 parts of tartaric acid, in a sufficient quantity of hot water, and carefully neutralised with potash, forms a clear solution, which may be boiled and mixed with any quantity of water without becoming turbid: the white precipitate which forms in it on the addition of a little more potash, especially on heating, is redissolved by a larger quantity of potash (R. Schneider).

When protochloride of tin is heated with a mixture of hydrochloric and sulphurous acids, a yellow precipitate of bisulphide of tin is formed: $6SnCl + 2SO_2 + 4HCl = SnS_2 + 5SnCl_2 + 4HO$. This reaction serves as a test for sulphurous acid.

The protochloride of tin is used in calico-printing, not only as a mordant, but also as a deoxidising agent, particularly to deoxidise indigo, and to reduce to a lower state of oxidation and discharge the sesquioxides of iron and manganese fixed upon cloth.

Protochloride of tin and potassium; $SnCl.KCl$.—Protochloride of tin forms a double salt with chloride of potassium, and also with chloride of ammonium, which compounds crystallise in the anhydrous state, and also with 3 eq. of water, or, according to Rammelsberg, with only 1 equivalent.

Anhydrous protochloride of tin fused in ammoniacal gas, absorbs half an equivalent of that gas, according to Persoz, forming $2SnCl.NH_3$, or rather perhaps $SnCl.(NH_3Sn)Cl$.

Protiodide of tin, SnI, is formed by heating a mixture of granulated tin and iodine. It is obtained in beautiful shining yellowish red prisms by gently boiling concentrated hydriodic acid with strips of tinfoil in a long glass tube for a day, or more readily by heating the acid with the tin in a sealed glass tube to a temperature of 248°, or at most 302° for an hour; after cooling, the remaining portion of tin is found to be covered with crystals. When tinfoil and iodide of amyl were heated together in a sealed tube for a day to 356°, the tinfoil became covered with yellowish-red quadratic octohedrons at the part where the tube cooled most quickly; but at the part which was immersed in the oil-bath, and therefore cooled more slowly, the metal was covered with sulphur-yellow prisms, which became yellowish-red when taken out (Wöhler). Stannous iodide was found by Boullay, jun., to form double salts with other iodides, particularly with the iodides of the alkaline and earthy metals, in which two atoms of the stannous iodide are combined with one of the other iodide.

Carbonic acid does not combine with either of the oxides of tin.

Protosulphate of tin, $SnO.SO_3$.—Tin dissolves in sulphuric acid, concentrated or a little diluted, yielding a saline mass, which forms a brown solution in water and deposits small crystalline needles on cooling.

Protonitrate of tin, $SnO.NO_5$, is obtained by dissolving hydrated protoxide of tin in nitric acid; the solution cannot be concentrated and is easily altered.

Tartrate of potash and tin, $KO.SnO.(C_8H_4O_{10})$ *or* $C_8H_4(KSn)O_{12}$.—Bitartrate of potash dissolves protoxide of tin, and forms a very soluble salt of potash and tin, which, like most of the tartrates, is not precipitated either by caustic alkalies or by alkaline carbonates. An addition of bitartrate of potash is occasionally made to the solution of tin used in dyeing.

Sesquioxide of tin, Sn_2O_3.—Was obtained by M. Fuchs, by diffusing recently precipitated sesquioxide of iron in a solution of protochloride of tin containing no excess of acid, and afterwards boiling the mixture. A double decomposition occurs, in which sesquioxide of tin precipitates, and protochloride of iron is retained in solution:

$$2SnCl + Fe_2O_3 = Sn_2O_3 + 2FeCl.$$

The sesquioxide thus obtained is a slimy grey matter, and usually yellow from adhering oxide of iron. Ammonia dissolves it easily, and without residue, a character which distinguishes this oxide from the protoxide of tin, the latter being insoluble, or nearly so, in that menstruum. Sesquioxide of tin is dissolved by concentrated hydrochloric acid; the taste of the solution is not metallic. It is distinguished from a salt of the bioxide of tin, by producing the purple precipitate with chloride of gold. A sesquisulphide exists, corresponding with this oxide. The salts of sesquioxide of tin have not been examined.

Bioxide of tin, Stannic oxide, SnO_2, 74·82 *or* 935·25.—This constitutes the common ore of tin, which is generally crystallised. The crystals of *tin-stone* are sometimes brownish-yellow and translucent, at other times dark brown and almost black, and contain small quantities of the protoxides of iron and manganese. Their primitive form is an obtuse octohedron with a square base; their density from 6·92 to 6·96. Bioxide of tin in this state does not dissolve in acids, unless previously ignited with an alkali. Anhydrous stannic oxide may be obtained in colourless crystals derived from a right rhomboïdal prism, which scratch glass, and have a density of 5·72, by decomposing vapour of bichloride of tin with water at a red heat. These crystals are isomorphous with one of the native varieties of titanic acid (brookite), whereas the crystals of native tinstone are isomorphous with another variety of titanic acid (rutile).

Bioxide of tin is susceptible of two modifications called *stannic* and *metastannic* acid, distinguished from one another by the proportions of water and metallic oxide with which they combine.

Stannic acid, or *Hydrated stannic oxide,* $SnO_2.HO$, is obtained by decomposing bichloride of tin with water, or by precipitating a soluble stannate with an acid. It is white, gelatinous, insoluble in water, but dissolves readily in dilute acids. A moderate heat converts it into metastannic acid. At a red heat, it gives off all its water, and becomes very hard.

Solutions of stannic oxide in acids (the hydrated bichloride for example), are decomposed by *zinc* and *cadmium,* the tin being precipitated in an arborescent form. *Hydrosulphuric acid* and *sulphide of ammonium* throw down the yellow bisulphide soluble in alkalies and in sulphide of ammonium. *Ammonia* throws down a white bulky hydrate, soluble with some turbidity in a large excess of ammonia. The presence of tartaric acid prevents the precipitation. *Potash* throws down a white bulky hydrate (probably containing potash), easily soluble in excess. *Carbonate of potash* gives a white precipitate, consisting, according to Fremy, of stannate of potash, which dissolves in excess of the reagent, but separates completely after a while. *Bicarbonate of potash* and *sesquicarbonate of ammonia* throw down the hydrated oxides, insoluble in excess of the reagent. Chloride of gold gives no precipitate with stannic salts.

All salts of tin are easily reduced to the metallic state when heated on charcoal before the blowpipe with carbonate of soda or cyanide of potassium.

The compounds of stannic acid with bases are represented by the general formula $MO.SnO_2$. The stannates of the alkalies crystallise readily, and may be obtained in the anhydrous state. They are prepared by dissolving stannic acid in alkalies, or by calcining metastannic acid or the metastannates in contact with an excess of base. *Stannate of potash,* $KO.SnO_2 + 4HO$, is white, very soluble in water, insoluble in alcohol; it crystallises in oblique rhomboïdal prisms, which are transparent, sometimes very large, and slowly absorb moisture from the air. It has a caustic taste and strong alkaline reaction. Water appears to decompose it after a while into potash and metastannate of potash. It is precipitated from its solution by nearly all soluble salts, even by those of potash, soda and ammonia. *Stannate of soda,* $NaO.SnO_2 + 4HO$, resembles the potash-salt, and is obtained in a similar manner. It crystallises in hexagonal tables, dissolves in cold more readily than in hot water, is insoluble in alcohol, and has a strong alkaline reaction (Fremy).

The stannates of all other bases are insoluble in water, and may be formed by double decomposition. The sesquioxide of tin may be regarded as a stannate of stannous oxide, $SnO.SnO_2$ (Fremy).

Metastannic acid, Sn_5O_{10}.—Tin treated with strong nitric acid is completely transformed into a white powder, which, when dried in the air at ordinary temperatures, contains $Sn_5O_{10}.10HO$; after being heated for some time to 212°, it is reduced to $Sn_5O_{10}.5HO$. It is white, crystalline, insoluble in water, and in dilute nitric acid and sulphuric acid. Monohydrated sulphuric acid dissolves it in considerable quantity, forming a compound which is not decomposed by water or alcohol. It dissolves in dilute hydrochloric acid, forming a liquid, which, when treated with excess of acid, yields a white amorphous precipitate, differing considerably from hydrated bichloride of tin. Metastannic acid also combines with certain organic acids. The acid prepared with nitric acid is completely insoluble in ammonia, but when dissolved in potash and precipitated by an acid, it becomes gelatinous and soluble in ammonia; in that state, it contains more water than in the crystalline state; but by the slightest desiccation, or even by boiling for a few minutes, it gives up part of its water, and is reconverted into the modification insoluble in ammonia. Other hydrates of metastannic acid appear also to exist, possessing different properties.

The *metastannates* are represented by the general formula (MO.4HO.) Sn_5O_{10}. They can only exist in the hydrated state, being decomposed when deprived of their basic water. The potash and soda-salts, heated with excess of base, are transformed into stannates. They are soluble in basic water. The other metastannates are insoluble, and are obtained by double decomposition. *Metastannate of potash,* (KO.4HO). Sn_5O_{10}, is prepared by dissolving metastannic acid in cold potash; it may be precipitated in the solid state by adding pieces of potash to the liquid. It is gummy, uncrystallisable, and strongly alkaline. At a red heat, it gives off its water and is decomposed; the calcined mass, digested in water, yields up all its alkali and leaves insoluble metastannic acid. The *soda-salt,* (NaO.4HO).Sn_5O_{10}, closely resembles the potash-salt, but is crystalline, dissolves slowly in water, and is decomposed by boiling water. *Metastannate of stannous oxide,* (SnO.4HO).Sn_5O_{10}, is obtained by placing metastannic acid in contact with protochloride of tin. It is yellow, and insoluble in water; when heated in contact with the air, it is transformed into anhydrous stannic acid (Fremy).

Oxide of tin is employed in the preparation of the white glass known as enamel; and the ignited and finely levigated oxide forms *jeweller's putty,* which is used in polishing hard objects. The hydrated oxide resembles alumina in forming insoluble compounds with the organic colouring matters; hence its salts are much prized as mordants.

Bisulphide of tin, Stannic sulphide, SnS_2, is precipitated from stannic salts, of a dull yellow colour, by hydrosulphuric acid gas. Prepared in the dry way, by igniting a mixture of stannic oxide, sulphur, and sal-ammoniac in a covered crucible, it forms the *aurum musivum* or *mosaic gold* of the alchemists. In this operation, the sal-ammoniac is indispensable, although it seems to serve no other purpose than to prevent the elevation of temperature which results from the sulphuration. Mosaic gold when well prepared has the yellow colour of gold, and consists of brilliant translucent scales, which are soft to the touch. No acid dissolves it, except aqua-regia. It is decomposed by dry chlorine, yielding the compound $SnCl_2.SCl_2$.

Bichloride of tin, Permuriate of tin, Stannic chloride, $SnCl_2$; 129·82 *or* 1622·75.—The anhydrous bichloride of tin, known as the fuming liquor of Libavius, is procured by distilling, at a gentle heat, a mixture of 4 parts of corrosive sublimate and 1 part of tin in filings, or tin amalgamated with a little mercury, and then reduced to powder. A colourless, highly limpid liquid is found in the condenser, which fumes strongly in humid air. The bichloride boils at 248°; the density of its vapour, observed by Dumas, is 9·1997. It forms a solid saline mass with one third of its weight of water, and dissolves in a larger quantity of water. The same salt is obtained in solution, by conducting a stream of chlorine gas into a strong solution of the protochloride of tin, till the latter is saturated, which is shown by the solution ceasing to precipitate mercury from a solution of corrosive sublimate. A solution of this salt extensively used in dyeing, and known as the nitromuriate of tin, is generally prepared by oxidising crystallised protochloride of tin with nitric acid; or by dissolving tin in a mixture of hydrochloric and nitric acids, avoiding any considerable elevation of temperature.

Ammonio-bichloride of tin, $SnCl_2.NH_3$ *or* $(NH_3Sn)Cl_2$.—Anhydrous bichloride of tin absorbs ammoniacal gas, and forms a white powder, which may be sublimed without decomposition; after sublimation it is entirely soluble in water (Rose).

Chlorosulphide of tin, $SnS_2.2SnCl_2$. — Hydrosulphuric acid gas is rapidly absorbed by bichloride of tin, with formation of hydrochloric acid gas:

$$3SnCl_2 + 2HS = SnS_2.2SnCl_2 + 2HCl.$$

The compound obtained by perfect saturation with hydrosulphuric acid is a yellowish or reddish liquid, heavier than water. When heated, it gives off bichloride of tin, and leaves the bisulphide (Dumas).

Bichloride of tin and sulphur, $SnCl_2.2SCl_2$. — Formed by the action of chlorine gas on bisulphide of tin at ordinary temperatures:

$$SnS_2 + 6Cl = SnCl_2.2SCl_2.$$

Large yellow crystals, which fuse when heated, and sublime without decomposition; they fume in the air more strongly than the bichloride.

Bichloride of tin with Pentachloride of phosphorus, $2SnCl_2.PCl_5$. —When a mixture of the last-described compound with terchloride of phosphorus is moderately heated in a stream of hydrochloric acid gas, a rapid action takes place, and this compound is formed, together with other products:

$$2(SnCl_2.2SCl_2) + 3PCl_3 = 2SnCl_2.PCl_5 + 2PCl_5 + 2S_2Cl.$$

If the retort in which the action takes place is connected with a receiver surrounded with ice, a pasty, yellowish mass collects in the receiver, and an amorphous white body remains in the retort. On heating the yellowish mass to between 212° and 250°, dichloride of sulphur escapes, and there remains a mixture of pentachloride of phosphorus with the double chloride, identical, in fact, with the amorphous white mass in the retort. On heating this mixture to a temperature between 284° and 320°, the pentachloride of phosphorus is also driven off, leaving the double chloride, which sublimes between 392° and 428°, in highly lustrous colourless needles, which, however, soon crumble to an amorphous powder, even when kept in close vessels. The compound fumes strongly in the air, and rapidly absorbs water, being thereby converted into transparent colourless crystals containing water of crystallisation.*

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* Casselmann, Ann. Ch. Pharm. lxxxiii. 257.

Bichloride of tin with Oxychloride of phosphorus, $2SnCl_2 + PO_2Cl_3$. — Obtained by the action of oxychloride of phosphorus on bichloride of tin: if an excess of either substance is present, the compound separates in large isolated crystals. It has a peculiar odour, melts at 131°, and boils at 356°, and distils without alteration if kept from contact with moist air. It fumes in the air and is decomposed by water. When oxychloride of phosphorus comes in contact in a close vessel with the compound $SnCl_2.2SCl_2$, the whole dissolves, forming a yellowish liquid, from which, after a while, the compound $2SnCl_2 . PO_2Cl_3$ crystallises; and above the crystals there remains a yellow liquid, probably SCl_2 (Casselmann).

Bichloride of tin with Phosphuretted hydrogen, $3SnCl_2.PH_3$. — These two bodies unite without production of hydrochloric acid; the compound is solid (Rose).

Bichloride of tin with potassium, $SnCl_2.KCl$. — The solution of bichloride of tin, when mixed with an equivalent quantity of chloride of potassium and evaporated, yields this double salt in anhydrous regular octohedrons having a vitreous lustre. A similar double salt is formed with chloride of ammonium.

A *sulphate* and *nitrate of bioxide of tin*, have been crystallised; this base forms no carbonate.

Both the *sulphide* and *bisulphide of tin* act as sulphur-acids, combining with alkaline sulphide. The bisulphide of tin dissolves with digestion in sulphide of sodium, and the concentrated solution yields fine crystals of the salt, $2NaS.SnS_2 + 12HO$. By gradually adding tin to melted pentasulphide of sodium, treating the resulting mass with water, and then filtering and evaporating, yellowish octohedral crystals are obtained, containing $NaS.SnS_2 + 2HO$.* The bisulphide of tin is found combined with the subsulphides of copper and iron, forming *tin pyrites*, a rare mineral, $2Fe_2S.SnS_2 + 2Cu_2S.SnS_2$.

Alloys of tin. — Tin alloyed with small quantities of antimony, copper, and bismuth, forms the best kind of pewter, possessing the peculiar whiteness of metallic tin. The most fusible compound of tin and bismuth is that of an atom of each metal, Bi.Sn; it melts at 289·4° (Rudberg). When the metals are mixed in other ratios, a portion first congeals at a higher temperature, separating from the compound mentioned, which remains liquid till the temperature falls to 289·4°. Although tin precipitates copper from its solutions in acids, yet it is possible to precipitate tin upon copper, and to cover the latter with tin, as is proved by the tinning of pins. Tin is dissolved in a mixture of 1 part of bitartrate of potash, 2 of alum, 2 of common salt, and a certain quantity of water, and the pins which consist of brass wire are introduced at the boiling temperature. The pins undergo no change in this liquor, supposing it to contain no undissolved tin, but the moment a fragment of tin touches the pins, all those in contact with each other are tinned. Dr. Odlings finds that pure copper boiled in a moderately dilute and rather acid solution of stannous chloride, also becomes coated with tin.*

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* Kühn, Pogg. Ann. lxxxv. 293.

ESTIMATION OF TIN, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Tin is estimated in the state of bioxide, a compound which contains 78·62 per cent. of the metal. If the tin is united with other metals in the form of an alloy, the alloy must be treated with nitric acid of sp. gr. about 1·3. The tin is then converted into bioxide, while the other metals (with the exception of antimony) are dissolved by the acid. The oxide of tin must then be thoroughly washed, afterwards dried, ignited, and weighed. To insure complete oxidation, the alloy should be finely divided.

When the tin is in solution in hydrochloric acid (which is its usual solvent) it must first be precipitated as a sulphide by hydrosulphuric acid, and the sulphide then converted into bioxide by roasting in an open porcelain crucible, a small quantity of nitric acid being added to insure complete oxidation.

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* Chem. Soc. Qu. J. ix. 291.

Precipitation by hydrosulphuric acid serves also to separate tin from all metals which are not thrown down by that reagent from their acid solutions.

From *cadmium, copper,* and *lead,* tin may be separated by treating the solution with a slight excess of ammonia, and then adding sulphide of ammonium containing excess of sulphur. All the metals are thereby converted into sulphides, but the sulphide of tin dissolves, while the others are left undissolved.

Volumetric estimation of tin. — The following method of estimating the amount of tin in the commercial protochloride is given by Dr. Penny*; it is based on the conversion of protochloride of tin into bichloride by the action of chromic acid in presence of free hydrochloric acid:

$$3SnCl + KO.2CrO_3 + 7HCl = 3SnCl_2 + KCl + Cr_2Cl_3 + 7HO.$$

The solution of the tin-salt is mixed with a sufficient quantity of hydrochloric acid and gently heated, and a solution of bichromate of potash gradually added, till a drop of the liquid added to acetate of lead (a solution of 1 part of that salt in 8 parts of water being scattered in large drops on a porcelain plate) produces a faint yellow colour; or till the liquid produces a dark brown or red colouring in an acidulated mixture of sulphocyanide of potassium and a pure protosalt of iron. With the commercial solution of the protochloride of tin, the contrary method is adopted; that is to say, the tin solution, diluted and reduced to a definite volume, is poured into a solution of bichromate of potash containing a known weight of that salt. Penny finds, by direct experiments, that 83·2 parts of pure bichromate of potash correspond to 100 parts of tin.

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* Chem. Soc. Qu. J. iv. 249.

SECTION II.

TITANIUM.

Eq. 24·33 *or* 303·7; Ti.

THIS metal was discovered in 1791, by Mr. Gregor of Cornwall, and afterwards by Klaproth, who gave it the name titanium. In the form of titanic acid it constitutes several minerals, as rutile, anatase, menachanite, &c.; and as titanate of protoxide of iron, it forms ilmenite and other species.

When titaniferous iron-ores are smelted in the blast furnace, small cubic crystals of a bright copper colour are found on the slag which adheres to the lower part of the furnace. These crystals were long supposed to be metallic titanium; but Wöhler* has shown that they also contain carbon and nitrogen, being, in fact, a compound of cyanide of titanium with nitride of titanium, $CyTi.3NTi_3$. Pure titanium is obtained by heating the double fluoride of potassium and titanium with potassium in a covered crucible. The metal is then set free with vivid incandescence, and the fluoride of potassium may be removed by washing with water. Titanium thus obtained is a dark green, heavy, amorphous powder, which does not exhibit any shade of copper colour, even after pressure; under the microscope it appears as a cemented mass, having the colour and lustre of iron. Metallic titanium is also obtained by mixing titanic acid with one-sixth of its weight of charcoal and exposing it to the strongest heat of a wind-furnace. It was thus obtained in the form of a copper-coloured or gold-coloured powder by Vauquelin, Lampadius, and others; but possibly the charcoal which they used may have contained nitrogen, and that element united with the reduced metal.

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* Ann. Ch. Pharm. lxxiii. 34.; Chem. Soc. Qu. J. ii. 352.

Pure titanium (prepared from the double fluoride) burns with great splendour when heated in the air, and, if sprinkled into a flame, is consumed, with brilliant scintillations, at a considerable distance above the point of the flame. When heated to redness in oxygen-gas, it burns with a splendour resembling a discharge of electricity. In chlorine-gas it exhibits similar phenomena, requiring also the aid of heat to set it on fire. Mixed with red lead and heated, it burns with such violence that the mass is thrown out of the vessel, with loud detonation. Titanium does not decompose water at ordinary temperatures, but on heating the water to the boiling point, hydrogen begins to escape. Warm hydrochloric acid dissolves titanium with brisk evolution of hydrogen. Ammonia added to the solution throws down a black oxide; and, on heating the liquid, hydrogen is evolved, and the precipitate first turns blue, and is afterwards converted into white titanic acid.

Titanium forms three compounds with oxygen: viz. the *protoxide*, TiO, whose composition is, however, doubtful; the *sesquioxide*, Ti_2O_3; and *titanic acid*, TiO_2.

Protoxide of titanium, TiO, 32·33. *or* 403·7 — Is formed when titanic acid is exposed in a charcoal crucible, to the highest temperature of a wind-furnace. Where the acid was in contact with the charcoal, a thin coating of metallic titanium is formed; but within, it is changed into a black mass, which is insoluble in all acids, and not otherwise affected by them, and is oxidated with difficulty when heated in contact with air, or by fusion with nitre. Protoxide of titanium is also obtained by the moist way, in the form of a deep purple powder, when a fragment of zinc or iron is introduced into a solution of titanic acid in hydrochloric acid; but it alters so quickly by absorption of oxygen, that no opportunity has yet been obtained of studying its properties. The composition assigned to it above is, therefore, hypothetical. The blue powder is, perhaps, a compound of protoxide of titanium with oxide of zinc or iron.

Sesquioxide of titanium, Ti_2O_3.—When anhydrous titanic acid is strongly ignited in a current of hydrogen gas, it becomes black and loses considerably in weight. From a determination of the actual loss of weight, Ebelmen concludes that sesquioxide of titanium is produced. The residue is not acted upon by nitric or hydrochloric acid, but dissolves in sulphuric acid, forming a violet solution.*

Titanic acid, TiO_2, 40·33 *or* 503·7.—In the mineral rutile, titanic acid is crystallised in the form of tinstone, the link by which tin is connected with titanium. Again, ilmenite and other varieties of titanate of iron, $FeO.TiO_2$ are isomorphous with sesquioxide of iron; and thus tin comes to be connected through titanium with the last order of metals. But titanic acid is dimorphous, and crystallises, in anatase, in an unconnected form. The best method of obtaining pure titanic acid is to fuse titanate of iron, reduced to powder and levigated with sulphur. The sulphur has no action upon the titanic acid, but converts the protoxide of iron into a sulphide of iron, which is dissolved by hydrochloric acid. If iron is still retained by the titanic acid, the latter is heated in a stream of hydrosulphuric acid gas, by which every particle of iron is converted into sulphide, and then removed by hydrochloric acid.

Titanic acid is a white powder, which acquires a yellow tint by exposure to a high temperature; it is infusible and insoluble in water. Titanic acid is considerably analogous in properties to silica; like that acid it has a soluble modification, formed by igniting titanic acid with an alkaline carbonate, which is soluble in dilute hydrochloric acid. The acid solution of titanic acid gives an orange-red precipitate with an infusion of gall-nuts, which is characteristic of titanic acid.

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* Ann. Ch. Phys. [3.] xx. 385.

On neutralising the acid solution with ammonia, the soluble modification of titanic acid is thrown down as a white gelatinous precipitate. When this precipitate is dried and heated, it glows, and the titanic acid is then no longer soluble in acids. When a solution of bichloride of titanium, or of the sulphate of titanic acid in water, is boiled for some time, titanic acid precipitates in the insoluble modification.

Titanic acid mixed with borax, or better with phosphorus-salt, forms in the outer blowpipe-flame a colourless glass, but in the inner flame, a glass which is yellow while hot, but assumes a violet colour on cooling. The same character is exhibited by those salts of titanic acid whose bases do not themselves impart any colour to the bead. If the titanic acid contains iron, the colour of the bead is brown-red or blood-red instead of violet. Many titanates yield the blue colour only with phosphorus-salt, not with borax. The colour is produced more readily by heating the substance on charcoal than on platinum wire. The above characters suffice to distinguish titanic acid from all other substances.

Bisulphide of titanium, TiS_2, was discovered by Rose, who formed it by passing the vapour of bisulphide of carbon over titanic acid, in a porcelain tube maintained at a bright red heat.

Bichloride of titanium, $TiCl_2$, was formed by Mr. George of Leeds, by transmitting chlorine over metallic titanium at a red heat. It is a transparent colourless liquid, resembling bichloride of tin, and boiling a little above 212°. The density of its vapour is 6·615 (Dumas). Bichloride of titanium combines with ammonia, and forms a white saline mass, $TiCl_2.2NH_3$. Metallic titanium is most easily obtained by heating this compound to redness. Bichloride of titanium also absorbs phosphuretted hydrogen, and forms a dry brown powder. From this compound when heated, a lemon-yellow sublimate rises, which Rose found to contain 3 atoms of bichloride of titanium, combined with 1 atom of a compound of phosphuretted hydrogen and hydrochloric acid, analogous to sal-ammoniac, but which could not be isolated. Bichloride of titanium combines with the alkaline chlorides, forming double salts, which are colourless and capable of crystallising. It also combines with chloride of cyanogen, forming a yellow crystalline compound containing $CyCl.2TiCl_2$, and with anhydrous hydrocyanic acid, forming the compound $HCy.TiCl_2$, a yellow pulverulent substance which sublimes below 212°, in transparent, shining, lemon-yellow crystals.

Bromide of titanium, $TiBr_2$, is obtained by passing bromine vapour over an intimate mixture of titanic acid and carbon, heated to bright redness, and distilling the resulting brown liquid with excess of mercury to remove free bromine. It is an amber-yellow crystalline body of specific gravity 2·6. It melts at 102°, and boils at 356°. It attracts moisture with the greatest avidity, and is converted into titanic and hydrobromic acids (F. B. Duppa).

A volatile *bifluoride of titanium*, TiF_2, was obtained by Unverdorben, by distilling titanic acid in a platinum apparatus with fluor spar in powder and fuming sulphuric acid.

A definite *sulphate of titanic acid*, $TiO_2 . SO_3$, is obtained by dissolving titanic acid in sulphuric acid, and evaporating to dryness at a heat below redness.

Nitrides of titanium.—H. Rose, by heating the double chloride of titanium and ammonium in ammoniacal gas, or by heating the ammonio-chloride of titanium, $2NH_3 . TiCl_2$, with sodium, obtained a copper-coloured substance which he supposed to be metallic titanium, but which Wöhler has shown to consist of nitride of titanium, Ti_3N_2, or more probably $Ti_6N_4 = 3TiN . Ti_3N$; it contains 28 per cent. of nitrogen. This compound is redder than the cubic crystals of the blast-furnaces, which have a tinge of yellow. Another nitride of titanium, TiN, is produced when titanic acid is strongly heated in a stream of ammoniacal gas. Its powder is dark violet with a tinge of copper-colour; in small pieces it exhibits a violet copper-colour and metallic lustre. A third nitride, Ti_5N_3, or more probably $2TiN . Ti_3N$, is formed when Rose's titanium is subjected to the action of a stream of hydrogen at a strong red heat. It has a brassy or almost gold-yellow colour and a metallic lustre. It is also obtained (mixed however with carbon) when titanic acid is heated to redness in a stream of cyanogen gas or hydrocyanic acid vapour; no cyanide of titanium is formed in this reaction. All these three nitrides of titanium sustain without decomposition, a temperature at least equal to that of melting silver. Mixed in the state of powder with the oxides of copper, lead, or mercury, and heated, they emit a lively sparkling flame, and reduce the oxides to the metallic state. When fused with hydrate of potash, they give off ammoniacal gas (Wöhler).

Nitrocyanide of titanium, $C_2NTi . 3Ti_3N$. — This is the copper-coloured compound already spoken of as occurring in the iron furnaces, and formerly mistaken for metallic titanium. Its formation appears to be connected with that of cyanide of potassium, so constantly observed in the blast-furnaces. It sometimes occurs in very large masses; in a furnace at Rübeland in the Hartz, a mass of it was found, weighing 80 pounds. This compound forms cubic crystals harder than quartz, and of specific gravity 5·3. It contains 18 per cent. of nitrogen and 4 of carbon. In its chemical characters, it resembles the nitrides just described, giving off ammonia when heated with potash, and reducing the oxides of lead, copper, and mercury, when heated with them. A similar product may be formed by placing a mixture of titanic acid and ferrocyanide of potassium in a well closed crucible, and exposing it for an hour to a heat sufficient to melt nickel. (Wöhler.)

ESTIMATION OF TITANIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Titanium is always estimated in the form of titanic acid. This compound is best precipitated from its solutions in acids by ammonia, which throws it down in the form of a very bulky precipitate, resembling hydrate of alumina. A great excess of ammonia must be avoided, as it would redissolve a small portion of the titanic acid. The precipitate after ignition contains 60 per cent. of titanium.

If the titanic acid, after precipitation by ammonia, is to be redissolved in acids, which is sometimes necessary in order to separate it from other metals, great care must be taken in the precipitation to avoid all rise of temperature, and the precipitate must be washed with cold water, because heat has the effect of rendering titanic acid more or less insoluble in acids.

Titanic acid may also in some cases be separated from its acid solutions by boiling; from the solution in sulphuric acid, complete precipitation is effected by this method; but when hydrochloric acid is the solvent, a small portion of titanic acid always remains in solution after boiling.

Protoxide of titanium is precipitated from its solutions by ammonia, and the precipitate, after standing from 24 to 36 hours, is converted, with evolution of hydrogen, into titanic acid, in which form it may be estimated.

From the *alkalies* and *alkaline earths*, titanic acid may be separated by ammonia, the solution in the latter case being carefully excluded from the air. Baryta may also be separated by sulphuric acid.

Titanic acid is separated from *magnesia* by boiling, if the two are dissolved in sulphuric acid, and by precipitation with carbonate of baryta, when hydrochloric acid is the solvent.

The separation from *alumina* and *glucina* is also effected by boiling the sulphuric acid solution.

From the metals which are precipitated as sulphides by sulphide of ammonium, viz., *manganese, iron, cobalt, nickel,* and *zinc,* titanic acid is separated by mixing the acid solution with tartaric acid and excess of ammonia (which then forms no precipitate), and adding sulphide of ammonium, which precipitates everything but the titanic acid. The filtered solution is then evaporated to dryness, and the residue ignited in a platinum crucible to expel ammoniacal salts and burn away the carbon of the tartaric acid. As this carbonaceous matter is very difficult to burn, the ignition should either be performed in a muffle furnace, or a stream of oxygen should be very gently directed into the crucible. The residue consists of titanic acid, which may then be weighed.

From *cadmium, copper, lead,* and *tin,* titanium is easily separated by hydrosulphuric acid.

SECTION III.

CHROMIUM.

Eq. 26·8 *or* 335; Cr.

THIS metal, so remarkable for the variety and beauty of its coloured preparations, was discovered by Vauquelin in 1797, in the red mineral now known as chromate of lead. It has since been found in other minerals, more particularly *chrome-iron* ($FeO . Cr_2O_3$), a mineral which many countries possess in considerable quantity. It is from this ore that the compounds of chromium, used in the arts, are actually derived. The metal may be procured by the reduction of its oxide, in the usual way; but the reduction is as difficult as that of manganese. Chromium is a greyish-white metal, of density 5·9, very difficult to fuse, and not magnetic. It does not undergo oxidation in the air. It dissolves in hydrofluoric acid with evolution of hydrogen. Chromium is also obtained as a brown powder, when sesquichloride of chromium is heated in ammoniacal gas (Liebig).

Chromium forms several compounds with oxygen; viz. *protoxide of chromium*, or *chromous oxide*, CrO, isomorphous with ferrous oxide, &c.; *sesquioxide of chromium*, or *chromic oxide*, Cr_2O_3, isomorphous with ferric oxide and alumina; and *chromic acid*, CrO_3, isomorphous with sulphuric acid; also a *chromoso-chromic oxide*, Cr_3O_4, or $CrO.Cr_2O_3$, and four oxides intermediate between chromic oxide and chromic acid, which may, in fact, be regarded as chromates of chromic oxide; viz. *monochromate of chromic oxide*, or $Cr_2O_3.CrO_3 = Cr_3O_6$; the *bichromate*, $Cr_2O_3.2CrO_3 = Cr_4O_9$; the neutral chromate, $Cr_2O_3.3CrO_3 = Cr_5O_{12}$, and the acid chromate, $Cr_2O_3.4CrO_3 = Cr_6O_{15}$.

Protoxide of chromium, Chromous oxide, CrO; 34·8 or 435. —This oxide probably exists in chrome-iron, and in pyrope. It is precipitated in the form of a hydrate by the action of potash on a solution of the protochloride. The anhydrous protoxide has not yet been obtained. The hydrate is very unstable, decomposes water, even at ordinary temperatures, and if the air be not excluded by filling the apparatus with hydrogen, is converted, almost as soon as formed, into chromoso-chromic oxide Cr_3O_4, with evolution of hydrogen (Péligot). It is yellow when recently precipitated, brown when dry, and may be preserved unaltered in dry air. When ignited it gives off hydrogen, and the oxygen thereby liberated converts the remaining protoxide into sesquioxide (Moberg).

Hydrated chromous oxide is insoluble in dilute acids, but dissolves slowly in strong acids. The chromous salts are best prepared by mixing a solution of the protochloride with the corresponding potash or soda salts, access of air being carefully prevented. They are generally of a red colour, sometimes inclining to blue; dissolve but sparingly in cold water, but more readily in hot water. Like ferrous salts, they dissolve large quantities of nitric oxide, forming dark brown solutions.

Protochloride of chromium, Chromous chloride, CrCl; 62·3· *or* 778·75.—Obtained by passing hydrogen gas over perfectly anhydrous sesquichloride of chromium very gently heated, as long as hydrochloric acid gas continues to escape. The hydrogen must be previously freed from all traces of oxygen by passing it through a solution of protochloride of tin in caustic potash, then through tubes containing sulphuric acid and chloride of calcium, and lastly over red-hot metallic copper. The protochloride is also formed by passing dry chlorine gas over a red-hot mixture of charcoal and chromic oxide. The first method yields the protochloride in the form of a white, velvety substance, retaining the form of the sesquichloride from which it has been formed; the second method yields it in fine white crystals, usually mixed, however, with chromic oxide, chromic chloride, and charcoal.

Protochloride of chromium dissolves in water, with evolution of heat, forming a blue solution, which rapidly turns green when exposed to the air or to chlorine gas. With *potash* it forms a dark brown precipitate (yellow, according to Moberg, if the air be completely excluded) of hydrated chromous oxide, which, however, quickly changes to light brown chromoso-chromic oxide, with evolution of hydrogen. *Ammonia* forms a greenish white precipitate, without evolution of hydrogen. With ammonia and sal-ammoniac, a blue liquid is formed which turns red on exposure to the air. *Sulphide of ammonium* or *potassium* forms a black precipitate of chromous sulphide. The solution of protochloride of chromium is one of the most powerful deoxidising agents known. With a solution of *monochromate of potash*, it forms a dark brown precipitate of chromoso-chromic oxide, which, however, disappears on the addition of an excess of the protochloride, and forms a green solution. It precipitates *calomel* from a solution of corrosive sublimate. With *cupric salts*, it forms at first a white precipitate of cuprous chloride; but when added in excess throws down red cuprous oxide. It instantly converts *tungstic* *acid* into blue oxide of tungsten, and precipitates *gold* from the solution of the chloride.

Chromous carbonate is formed by adding a solution of the chloride to carbonate of potash; its precipitate is red or red-brown, if the alkaline solution is hot, but in the form of dense yellow or bluish green flakes, if it is cold; the precipitate appears, however, to have the same composition in all cases (Moberg).

Chromous sulphite is obtained by double decomposition in the form of a brick-red precipitate, which becomes bluish-green on exposure to the air (Moberg).

Chromous sulphate.—When the metallic powder obtained by treating sesquichloride of chromium with potassium is treated with dilute sulphuric acid, hydrogen is evolved, and a solution obtained which exhibits the characters of a chromous salt (Péligot).

Chromoso-chromic oxide, $Cr_3O_4 = CrO \,.\, Cr_2O_3$.—Formed when the protoxide comes in contact with water, and consequently at the moment of its precipitation by potash, from a solution of the protochloride. After washing with water and drying in vacuo, it has the colour of Spanish tobacco. It is but feebly attacked by acids. The hydrate is composed of $Cr_3O_4 \,.\, HO$; when heated, it is converted into chromic oxide with evolution of hydrogen.

Sesquioxide of chromium, Chromic oxide, 77·6 or 970.—This oxide exists in chrome-iron, but is not immediately derived from that mineral. When chromate of mercury, the orange precipitate obtained on mixing nitrate of mercury and chromate of potash, is strongly ignited, chromic oxide remains as a powder of a good green colour. Chromic oxide is also obtained, by deoxidising the chromic acid of bichromate of potash in various ways; by ignition with sulphur, for instance, or by igniting together 1 part of bichromate of potash with $1\frac{1}{2}$ parts of sal-ammoniac and 1 part of carbonate of potash, whereby chloride of potassium and sesquioxide of chromium, are formed, the chromic acid losing half its oxygen, which is converted into water by the hydrogen of the ammonia. Another process, interesting from affording the oxide in the state of crystals, is to pass the vapour of chlorochromic acid (CrO_2Cl) through a tube heated to whiteness, when oxygen and chlorine gases are disengaged, and chromic oxide attaches itself to the surface of the tube. The crystals have a metallic lustre, and are of so deep a green as to appear black; they have the same form as specular iron ore, a density of 5·21, and are as hard as corundum (Wöhler). The ignited oxide is not soluble in acids; heated with access of air, and in contact with an alkali, it absorbs oxygen and is converted into chromic acid. Fused with borax or other vitreous substances, sesquioxide of chromium produces a beautiful green colour; it is the colouring matter of the emerald, and is employed to produce a green colour upon earthenware. Sesquioxide of chromium (and not chromic acid) is also the colouring matter of *pink colour* applied to stoneware. This substance is formed by strongly igniting a mixture of 100 parts of bioxide of tin, 33 parts of chalk, and not more than one part of sesquioxide of chromium.*

To obtain the same oxide in the hydrated state, a solution of bichromate of potash is brought to the boiling point, and hydrochloric acid and alcohol added alternately in small quantities, till the solution passes from a red to a deep green colour, and no longer effervesces from escape of carbonic acid gas, on addition of either the acid or alcohol. In this experiment, the chromic acid liberated by the hydrochloric acid, is deprived of half its oxygen by the hydrogen and carbon of the alcohol, and the resulting sesquioxide of chromium is dissolved by the excess of hydrochloric acid present, and in fact converted into the corresponding sesquichloride of chromium. Many other organic substances may be used in place of alcohol in this experiment, such as sugar, oxalic acid, &c. The reduction may also be effected by hydrosulphuric acid or even by hydrochloric acid alone, if added in sufficient excess; in this last case, sesquichloride of chromium and chloride of potassium are then formed, and part of the chlorine escapes as gas; thus:

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* Malaguti, Ann. Ch. Phys. [3.] lxi. p. 433. Mr. O. Sims finds that sesquioxide of iron and bioxide of manganese may be substituted for oxide of chromium in pink colour, so that the coloration of that substance is of a very peculiar character.

$$KO.2CrO_3 + 7HCl = KCl + Cr_2Cl_3 + 7HO + 3Cl.$$

The oxide of chromium is precipitated from the green solution by ammonia, and falls as a pale bluish-green hydrate. The same oxide is obtained more directly, when to a boiling solution of bichromate of potash a hot solution of pentasulphide of potassium is added, the chromic acid then giving half its oxygen to the sulphur.

Hydrated chromic oxide is soluble in acids, and forms salts. It is also dissolved by potash and soda, but not to a great extent by ammonia. Its salts have a sweet taste, and are poisonous. The oxide itself becomes of a greener colour when dried, and loses water. A moderate heat affects its relations to acids, the sulphate of the heated (or green) oxide not forming a double salt, for instance, with sulphate of potash. When heated to redness, it glows, or undergoes the same change as zirconia, bioxide of tin, and many other hydrated oxides when made anhydrous; becomes denser, assumes a pure green colour, and ceases to be soluble in acids.

The salts of chromic oxide exhibit two different modifications, green and violet; some acids, *e. g.*, sulphuric and hydrochloric, produce both modifications; others only one. *Ammonia* produces, in solutions of the green salts, a bluish-gray precipitate, but in solutions of the violet salts, a greenish-gray precipitate, both of which, however, yield green solutions when dissolved in sulphuric or hydrochloric acid (Regnault); according to H. Rose, however, the precipitate is bluish-gray in both cases. The liquid above the precipitate has a reddish colour, and contains a small quantity of chromic acid. *Potash* and *soda* form similar precipitates, which dissolve in excess of the alkali, forming green solutions from which the chromic oxide is precipitated by boiling. The *alkaline carbonates* form greenish precipitates (violet by candle-light), which dissolve to a considerable extent in excess of the reagent. *Hydrosulphuric acid* forms no precipitate; *sulphide of ammonium* throws down the hydrated sesquioxide.

Zinc, immersed in a solution of chrome-alum or sesquichloride of chromium excluded from the air, gradually reduces the chromic salt to a chromous salt, the liquid after a few hours acquiring a fine blue colour, and hydrogen being evolved by decomposition of water. If the zinc be left in the liquid after the change of colour from green to blue is complete, hydrogen continues to escape slowly, and the liquid after some weeks or months, is found no longer to contain chromium, the whole of that metal being precipitated in the form of a basic salt, and its place taken by zinc. *Tin*, at a boiling heat, likewise reduces the chromic salt to a chromous salt, but only to a limited extent; and on leaving the liquid to cool after the action has ceased, a contrary action takes place, the protochloride of chromium decomposing the protochloride of tin previously formed, reducing the tin to the metallic state, and being itself reconverted into sesquichloride. *Iron* does not reduce chromic salts to chromous salts, but merely precipitates a basic sulphate of chromic oxide, or an oxychloride, as the case may be.*

Sesquioxide (and also the protoxide) of chromium, ignited with an alkaline carbonate, or better with a mixture of the carbonate and nitre, is converted into chromic acid, which unites with the alkali; and on dissolving the fused product in water, filtering if necessary, and neutralising with acetic acid, the characteristic reactions of chromic acid (p. 164.)

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* H. Loewel, Ann. Ch. Phys. [3.] xl. 42.

may be obtained with lead and silver-salts. An oxide of chromium fused with borax, in either blowpipe flame, yields an emerald-green glass. The same character is exhibited by those salts of chromic acid whose bases do not of themselves impart decided colours to the bead.

A *sesquisulphide of chromium*, Cr_2S_3, corresponding with the oxide, is obtained by exposing the latter, in a porcelain tube, to the vapour of bisulphide of carbon, at a bright red heat. It is a substance of a dark grey colour, which is dissolved by nitric acid.

Sesquichloride of chromium, Chromic chloride, Cr_2Cl_3; 160·1 or 2001·2.—This salt is obtained as a sublimate of a peach-purple colour, when chlorine is passed over a mixture of oxide of chromium and charcoal, ignited in a porcelain tube: or in the hydrated state by evaporating the solution of sesquichloride of chromium to dryness. The salt obtained by the latter process is a green powder containing $Cr_2Cl_3 + 9HO$. When heated, it gives off water and hydrochloric acid, and leaves a residue of oxychloride of chromium. Heated in a current of hydrochloric acid gas, it likewise parts with its water, and is converted into the violet anhydrous sesquichloride. The solution, evaporated in vacuo, leaves an amorphous mass which dissolves in water with evolution of heat, and consists of $Cr_2Cl_3 + 6HO$ (Péligot). Anhydrous sesquichloride of chromium is perfectly insoluble in cold water, and dissolves but very slowly in boiling water; but if to cold water in which the sesquichloride is immersed, there be added a very small quantity, even $\frac{1}{10000}$, of protochloride of chromium, a green solution is formed identical with that which is obtained by dissolving chromic oxide in hydrochloric acid (Péligot).

Chromic sulphate, $Cr_2O_3.3SO_3$; 197·6 or 247·0.—Chromic oxide is dissolved by sulphuric acid, but the salt does not crystallise. Chromic sulphate exhibits a violet and a green modification. The violet sulphate is obtained by leaving 8 parts of hydrated chromic oxide, dried at 212°, and 8 or 10 parts of strong sulphuric acid in a loosely stoppered bottle for several weeks. The solution, which is green at first, gradually becomes blue, and deposits a greenish blue crystalline mass. On dissolving this substance in water, and adding alcohol, a violet-blue crystalline precipitate is formed; and by dissolving this precipitate in very weak alcohol, and leaving the solution to itself for some time, small regular octahedrons are deposited, containing $Cr_2O_3 . 3SO_3 + 15HO$. The *green sulphate* is prepared by dissolving chromic oxide in strong sulphuric acid at a temperature between 122° and 140°; also by boiling a solution of the violet sulphate. The liquid, when quickly evaporated, yields a green crystalline salt, having the same composition as the violet sulphate. The green sulphate dissolves readily in alcohol, forming a blue solution; but the violet salt is insoluble in alcohol. The solution of the green sulphate is not completely decomposed by soluble baryta-salts at ordinary temperatures, a boiling heat being required to complete it; the violet sulphate, on the contrary, is deprived of all its sulphuric acid by baryta-salts at ordinary temperatures. When either the green or the violet sulphate is heated to 390°, with excess of sulphuric acid, a light yellow mass is obtained, which, when further heated, leaves a residue of anhydrous chromic sulphate, having a *red* colour. This anhydrous salt is completely insoluble in water, and dissolves with difficulty even in acid liquids.*

Chromic sulphate forms a crystallisable double salt with sulphate of potash, viz., *chrome-alum,* $KO . SO_3 + Cr_2O_3 . 3SO_3 + 24HO$. This salt is produced when a mixture of its constituent salts, with a little free sulphuric acid, is left to spontaneous evaporation. The best mode of preparing it is to mix three parts of a saturated solution of neutral chromate of potash, first with one part of oil of vitriol, and then with two parts of alcohol, which is to be added by small portions to the mixture of acid and chromate, and not to apply artificial heat. The chromic acid is thus deoxidised in a gradual manner, and large crystals of the double sulphate are slowly deposited (Fischer). The octohedral crystals of chrome-alum are of a dark purple colour, and of a beautiful ruby-red, when so small as to be transparent. The solution is bluish-purple, but when heated to 140° or 180° becomes green, and, according to Fischer, either deposits on evaporation a bright-green amorphous, difficultly soluble mass, or yields crystals of sulphate of potash, while green chromic sulphate remains in solution. According to Loewel*, on the contrary, the change of the purple into the green salt does not arise from a separation of the two simple salts, but merely from loss of water of crystallisation. A solution of chrome-alum, which has become green and uncrystallisable by heating, does not deposit any sulphate of potash even when concentrated; neither does that salt separate when the crystals are melted in a sealed tube; but the green liquid obtained by either of these processes yields, when heated to 77° and 86° in a dry atmosphere, a dark green mass containing $Cr_2O_3.3SO_3 + KO.SO_3$, with scarcely 6 eq. water (Loewel). The violet crystals containing 24 Aq., when left for several days in dry air at a temperature between 77° and 86°, give off 12 Aq., and assume a lilac colour. At 212°, another quantity of water goes off, and the crystals become green; and, by gradually raising the temperature to about 660°, the whole of the water may be expelled without causing the salt to melt. The anhydrous crystals are green, and dissolve without residue in boiling water, but at a temperature somewhat above 660°, they suddenly become greenish-yellow, without perceptible loss of weight, and are afterwards perfectly insoluble in water.

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* Regnault, Cours de Chimie.

Oxalate of chromium and potash, $3(KO.C_2O_3) + Cr_2O_3.3C_2O_3 + 6HO$. — This is another beautiful double salt of chromium,

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* Ann. Ch. Phys. [3.] xliv. 313.

It is easily prepared by the following process of Dr. Gregory:—One part of bichromate of potash, two parts of binoxalate of potash, and two parts of crystallised oxalic acid are dissolved together in hot water. A copious evolution of carbonic acid gas takes place, arising from the deoxidation of the chromic acid, at the expense of a portion of the oxalic acid; and nothing fixed remains, except the salt in question, of which a pretty concentrated solution crystallises upon cooling in prismatic crystals, which are black by reflected light, but of a splendid blue by transmitted light, when sufficiently thin to be translucent. The oxide of chromium is not completely precipitated from this salt by an alkaline carbonate; and it is remarkable that only a small portion of the oxalic acid is thrown down from it by chloride of calcium. When fully dried and then carefully ignited, this salt is completely decomposed, and leaves a mixture of chromate and carbonate of potash. The corresponding double oxalate of chromium and soda contains 9HO, according to Mitscherlich. In the analogous oxalate of ferric oxide and soda, the proportion of water appeared to the author to be 10HO.

The mineral *chrome-iron*, $FeO.Cr_2O_3$, crystallises in octohedrons, and corresponds with the magnetic oxide of iron, having the sesquioxide of iron replaced by sesquioxide of chromium. Its density is 4·5; it is about as soft as felspar, and infusible. When exposed to long-continued calcination, in contact with carbonate of potash, in a reverberatory furnace, the oxide of chromium of this compound absorbs oxygen, and combines as chromic acid with the potash, while the protoxide of iron becomes sesquioxide. The addition of nitre increases the rapidity of oxidation, but is not absolutely required in the process. A yellow alkaline solution of carbonate and chromate of potash is obtained by lixiviating the calcined matter, which is generally converted into the red chromate or bichromate of potash, by the addition of the proper quantity of sulphuric acid, the latter salt being more easily purified by crystallisation than the neutral chromate.

Chromic acid, CrO_3, 52·19 *or* 651·8.—This acid is not liberated from the chromates in a state of purity by any acid except the fluosilicic; it is also easily altered. Fluosilicic acid gas is conducted into a warm solution of bichromate of potash, till the potash is completely separated as the insoluble fluoride of silicon and potassium, which may be ascertained by testing a few drops of the solution with tartaric acid or chloride of platinum. The solution is evaporated to dryness by a steam heat, and the chromic acid redissolved by water; it gives an opaque, dull red solution. Chromic acid may also be obtained anhydrous and in acicular crystals, by distilling, in a platinum retort, a mixture of 4 parts of chromate of lead, 3 parts of finely pulverised fluor spar, and 7 parts of Nordhausen sulphuric acid; sulphate of lime is formed, together with perfluoride of chromium, the vapour of which is received in a large platinum crucible, covered with wet paper and used as a condenser. The perfluoride is decomposed by the aqueous vapour from the paper, being resolved into hydrofluoric acid and beautiful orange-red acicular crystals of chromic acid, which fill the crucible. A third and easier method of preparing chromic acid is to mix a solution of bichromate of potash, saturated between 122° and 140°, with 1½ times its volume of strong sulphuric acid, adding the acid by successive small portions. Bisulphate of potash is then formed, which remains in solution, and the liquid, as it cools, deposits the chromic acid in long red needles. These may be drained, first in a funnel, afterwards on a brick; then dissolved in water; the solution treated with a small quantity of chromate of baryta to remove the last portion of sulphuric acid; and the filtered liquid evaporated in vacuo. Chromic acid differs remarkably from sulphuric acid, in having but little affinity for basic water, so that it may be obtained anhydrous by evaporating its solution to dryness. Indeed, the chromate of water is not known to exist, even in combination, both the bichromate and terchromate of potash being anhydrous salts. The free acid is a powerful oxidizing agent, and bleaches organic colouring matters: chromic acid then loses half its oxygen, and becomes oxide of chromium. It is also converted into sesquichloride of chromium by hydrochloric acid, with evolution of chlorine:

$$2CrO_3 + 6HCl = Cr_2Cl_3 + 6HO + 3Cl;$$

and into sesquioxide by hydrosulphuric acid, with precipitation of sulphur:

$$2CrO_3 + 3HS = Cr_2O_3 + 3HO + 3S.$$

Sulphurous acid passed through a solution of chromic acid, or its salts, throws down a brown precipitate, consisting of monochromate of chromic oxide, or bioxide of chromium; $Cr_2O_3 . CrO_3 = 3CrO_2$. The other intermediate oxides, or chromates of chromic oxide mentioned on page 153., are formed by other imperfect reductions of chromic acid, or by the imperfect oxidation of chromic oxide. They are all brown substances, soluble in potash and in nitric acid. One of them, the bichromate, dissolves also without decomposition in hydrochloric and sulphuric acid; the others are reduced by hydrochloric acid to sesquichloride, with evolution of chlorine, and resolved by sulphuric acid into chromic acid and sulphate of chromic oxide.*

Chromic acid forms bibasic, monobasic, biacid, and a few tri-acid salts. The monochromates of the alkalies are yellow, the bichromates red; the chromates of the metals proper are bright yellow, red, or occasionally of some other colour. All chromates heated with oil of vitriol give off oxygen, and form sulphate of chromic oxide, together with another sulphate. When heated with hydrochloric acid, they give off chlorine and form sesquichloride of chromium, together with another metallic chloride. Heated in the anhydrous state with common salt and sulphuric acid, they give off red vapours of chlorochromic acid, which condense to a brownish red liquid. Similarly, when heated with fluor spar and sulphuric acid, they give off red vapours of terfluoride of chromium. A few only of the chromates, more particularly those of the alkalies, are soluble in water, but they all dissolve in nitric acid. Solutions of the alkaline chromates form a pale yellow precipitate with baryta salts; bright yellow with lead-salts; brick red with mercurous salts; and crimson with silver salts.

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* For a full account of these brown oxides, see the translation of Gmelin's Handbook, iv. 113.

Chromate of potash, Yellow chromate of potash, $KO.CrO_3$; 97·8 or 1222·5.—This salt is produced in the treatment of the chrome ore, but is seldom crystallised. It may be formed from the bichromate, by fusing that salt with an equivalent quantity of carbonate of potash; or by adding caustic potash to a red solution of the bichromate, till its colour becomes a pure golden yellow. The solution of chromate of potash has a great tendency to effloresce upon the sides of the basin when evaporated. Its crystals are of a yellow colour, anhydrous, and isomorphous with sulphate of potash. One hundred parts of water at 10° dissolve $48\frac{1}{3}$ parts of this salt; the solution preserves its yellow colour, even when diluted to a great degree.

Bichromate of potash, Red chromate of potash.—$KO.2CrO_3$; 148·6 or 1857·5.—This beautiful salt, of which a large quantity is consumed in the arts, crystallises in prisms or in large four-sided tables, of a fine orange-red colour. It fuses below a red heat, and forms on cooling a crystalline mass, the crystals of which have, according to Mitscherlich, the same form as those obtained from an aqueous solution; but this mass falls to powder as it cools, from the unequal contraction of the crystals in different directions. At 60°, water dissolves $\frac{1}{10}$ of its weight of this salt, and at the boiling point a considerably greater quantity.

Bichromate of chloride of potassium, Péligot's salt, $KCl.2CrO_3$.—This salt, which we are obliged to designate as if it contained chloride of potassium combined as a base with chromic acid, is formed by dissolving together, with the aid of heat, about three parts of bichromate of potash and four of concentrated hydrochloric acid, with a small quantity of water, avoiding the evolution of chlorine. It crystallises in flat red quadrangular prisms, and is decomposed by solution in pure water.

Terchromate of potash, $KO.3CrO_3$, is obtained crystallised when a solution of the bichromate is mixed with nitric acid, and evaporated. Bichromates of soda and silver exist which are anhydrous, like the bichromate of potash (Warington).

Chromate of soda, $NaO.CrO_3+10HO$.—By the evaporation of a concentrated solution of this salt, it is obtained in large fine crystals, having the form of glauber salt. The bichromate crystallises in thin, hyacinth-red, six-sided prisms, bevelled at the ends.

Chromate of ammonia, $NH_4O.CrO_3$ is prepared by evaporating a mixture of chromic acid with a slight excess of ammonia. It crystallises in lemon-yellow needles, very soluble in water, and having an alkaline reaction and pungent saline taste. When heated, they give off ammonia, water, and oxygen, and leave sesquioxide of chromium. The *bichromate,* $NH_4O.2CrO_3$, forms orange-yellow or reddish brown rhombic tables, which at a heat below redness are decomposed, with emission of light and feeble detonation, leaving the sesquioxide. It combines with chloride of mercury, forming crystalline compounds, containing $NH_4O.2CrO_3.HgCl+HO$, and $3(NH_4O.2CrO_3).HgCl$ (Richmond and Abel).* Rammelsberg has obtained an acid salt composed of $NH_4O.6CrO_3+10HO$.

Chromate of baryta, $BaO.CrO_3$ is a lemon-yellow powder obtained by precipitating a baryta-salt with an alkaline chromate.

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* Chem. Soc. Qu. J. iii. 139.

It is insoluble in water, but dissolves easily in nitric, hydrochloric, or chromic acid. When a baryta-salt is precipitated with neutral chromate of potash, and sulphuric acid added, the precipitate dissolves with partial decomposition, and on diluting with water, mixing the filtered solution with chromic acid, and evaporating in vacuo, neutral chromate of baryta first separates, then crystals of a *bichromate*, $BaO.2CrO_3+2HO$, and afterwards a double salt containing $2(BaO.3CrO_3.HO)+(KO.3CrO_3.HO)$. (Bahr.)*

Neutral chromate of lime, $CaO.CrO_3$, is obtained by treating carbonate of lime with aqueous chromic acid; and by treating the neutral salt with excess of chromic acid and evaporating, a *bichromate*, $CrO.2CrO_3 + 2HO$, is obtained. Chloride of calcium mixed with monochromate of potash, yields a double salt containing $5(CaO.CrO_3)+KO.CrO_3$. (Bahr.)

Chromate of magnesia forms, according to the author's observations, yellow crystals which are very soluble, and contain 5HO. It does not form a double salt with chromate of potash, as sulphate of magnesia does with sulphate of potash. It is remarked that the insoluble metallic chromates generally carry down portions of the neutral precipitating salts, or of subsalts, and their analysis is often unsatisfactory from that cause. When the magnesian chromates are compared with the sulphates of the same family, the former are found to have their water readily replaced by metallic oxides, but not by salts; so that subchromates with excess of oxide are numerous, while few or no double chromates exist.

Chromate of lead, $PbO.CrO_3$; 162·4 or 2030.—This compound, so well known as *chrome-yellow*, is obtained by mixing nitrate or acetate of lead with chromate or bichromate of potash. The precipitate is of a lighter shade from dilute than from concentrated solutions. It is entirely soluble in potash or soda, but not in dilute acids.

Subchromate of lead, $2PbO.CrO_3$, is of a red colour. It is formed when a solution of neutral chromate of potash, mixed with as much free alkali as it already contains, is added to a solution of nitrate of lead. But the finest vermilion-red subchromate is formed when one part of the neutral chromate of lead is thrown into five parts of nitre in a state of fusion by heat. Water dissolves the chromate and nitrate of potash in the fused mass, and leaves the subchromate of lead as a crystalline powder, (Liebig and Wöhler). An orange pigment may be obtained very economically, by boiling the sulphate of lead, which is a waste product in making acetate of alumina from alum by means of acetate of lead, with a solution of chromate of potash. The subchromate of lead forms a beautiful orange upon cloth, which is even more stable than the yellow chromate, not being acted upon by either alkalies or acids. One method of dyeing chrome-orange, is to fix the yellow chromate of lead first in the calico, by dipping it successively in acetate of lead and bichromate of potash, and then washing it. This should be repeated, in order to precipitate a considerable quantity of the chromate in the calico. A milk of lime is then heated in an open pan; and when it is at the point of ebullition, the yellow calico is immersed in it, and instantly becomes orange, being deprived of a portion of its chromic acid by the lime, which forms a soluble chromate of lime. At a lower temperature, lime-water dissolves the chromate of lead entirely, and leaves the cloth white.

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* J. pr. Chem. lx. 60.

Chromate of silver falls as a reddish brown precipitate when nitrate of silver is added to neutral chromate of potash. Dissolved in hot and concentrated solution of ammonia, it yields, on cooling, large well formed crystals, $AgO\,CrO_3+2NH_3$, isomorphous with the analogous ammoniacal sulphate and seleniate of silver.

Chlorochromic acid, CrO_2Cl, or $2CrO_3.CrCl_3$.—This is a volatile liquid, obtained by distilling, in a glass retort, at a gentle heat, 3 parts of bichromate of potash and 3½ parts of common salt, previously reduced to powder and mixed together, with 5 parts by water-measure of oil of vitriol, discontinuing the distillation when the vapours, from being of a deep orange-red, become pale — that change arising from watery vapour. The compound is a heavy red liquid, decomposed by water. The density of its vapour is 5·9.

Terfluoride of chromium, CrF_3, is obtained in the manner already mentioned under the preparation of chromic acid. It is a blood-red liquid. No corresponding terchloride of chromium has been obtained in an isolated state.

Perchromic acid, Cr_2O_7. — When peroxide of hydrogen dissolved in water is mixed with a solution of chromic acid, the liquid assumes a deep indigo-blue colour, but often loses this colour very rapidly, giving off oxygen at the same time. The same blue colour is formed by adding a mixture of aqueous peroxide of hydrogen and sulphuric or hydrochloric acid to bichromate of potash; but, in a very short time, oxygen is evolved, and a potash-salt, together with a chromic salt, left in solution. For each atom of $KO.2CrO_3$, four atoms of oxygen are evolved, provided an excess of HO_2 be present:

$$KO.2CrO_3 + O + 4SO_3 = KO.SO_3 + Cr_2O_3.3SO_3 + 4O.$$

The peroxide of hydrogen first gives up 1 at. O to the 2 at. of CrO_3, and forms Cr_2O_7; and this compound is subsequently resolved into Cr_2O_3 and 4O. With ether, perchromic acid forms a more stable blue mixture than with water, and in this state may be made to unite with ammonia and with certain organic bases, forming very stable compounds, from which stronger acids separate the blue acid.

ESTIMATION OF CHROMIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Chromium is usually estimated in the state of sesquioxide. When it exists in solution in that state, it may be precipitated by ammonia, care being taken to avoid a large excess of that reagent (which would dissolve a portion), and to heat the liquid for some time. The chromic oxide is then completely precipitated, and the precipitate, after washing and drying, is reduced by ignition to the state of anhydrous sesquioxide, containing 70·1 per cent. of the metal.

When chromium exists in solution in the state of chromic acid, it is best to precipitate it by a solution of mercurous nitrate; the mercurous chromate thereby thrown down yields by ignition the anhydrous sesquioxide. The chromic acid might also be precipitated and estimated in the form of a baryta or lead salt.

Chromic acid may also be estimated by means of oxalic acid, which reduces it to sesquioxide, being itself converted into carbonic acid. The quantity of carbonic acid evolved determines the quantity of chromic acid present, 3 eq. CO_2 corresponding to 1 eq. CrO_3, as shown by the equation:

$$2CrO_3 + 3C_2O_3 = Cr_2O_3 + 6CO_2.$$

The mode of proceeding is the same as that adopted for the valuation of black oxide of manganese (p. 17). If the object be merely to determine the quantity of chromium present, any salt of oxalic acid may be used; but if the alkalies are also to be estimated in the remaining liquid, the ammonia or baryta salt must be used.

Chromic oxide, in the state of neutral or acid solution, is easily separated from the *alkalies* or *alkaline earths*, by precipitation with ammonia, care being taken in the latter case to protect the liquid and precipitate from the air. The same method, with addition of sal-ammoniac, serves to separate chromic oxide from *magnesia*. The separation from the alkaline earths and from magnesia may also be effected by precipitating the whole with an alkaline carbonate, and igniting the precipitate with a mixture of carbonate of soda and nitre. The chromium is then converted into chromate of soda, which may be dissolved out, and the solution, after neutralisation with nitric or acetic acid, treated with mercurous nitrate as above.

From *alumina* and *glucina,* chromic oxide may be separated by treating the solution with excess of potash, and boiling the liquid to precipitate the chromic oxide. The separation is, however, more completely effected by fusing with nitre and carbonate of soda, treating the fused mass with water, adding an excess of nitric acid to dissolve anything that may be insoluble in water, and precipitating the alumina or glucina by ammonia.

Another method of converting chromic oxide into chromic acid, and thereby effecting its separation from the abovementioned oxides, is to treat the mixture with excess of potash, and heat the solution gently with bioxide of lead. The whole of the chromium is then converted into chromic acid, and remains dissolved as chromate of lead in the alkaline liquid; and on filtering from the excess of bioxide of lead, and any other insoluble matter that may be present, and supersaturating the filtrate with acetic acid, the chromate of lead is precipitated (Chancel).*

Chromic acid may be separated from the alkalies in neutral solutions by precipitation with mercurous nitrate; also by reducing it to chromic oxide with hydrochloric acid and alcohol, and precipitating by ammonia. From the *earths* it may also be separated by this latter method, or, again, by fusing with carbonate of soda, dissolving out with water, &c.

From *manganese, iron* (in the state of protoxide), *cobalt, nickel,* and *zinc,* chromium in the state of sesquioxide may be separated by agitation with carbonate of baryta, which precipitates the chromic oxide, leaving the protoxides in solution. The precipitate is then treated with dilute sulphuric acid, which dissolves the chromic oxide and leaves the baryta, and the filtrate treated with ammonia to precipitate the chromic oxide. Chromium may also be separated from all these metals, except manganese, by fusion with nitre and carbonate of soda, or with the carbonate alone if it is already in the form of chromic acid. Or, again, the separation may be effected by means of potash and bioxide of lead, according to Chancel's method above described.

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* Compt. rend. xliii. 927.

From *cadmium, copper, lead,* and *tin,* chromium is easily separated by hydrosulphuric acid.

When sesquioxide of chromium and chromic acid occur together in a solution, the chromic acid may be precipitated by mercurous nitrate, the solution being first completely neutralised, and the sesquioxide precipitated from the filtrate by ammonia, which at the same time throws down a mercury-compound, to be afterwards separated from the chromic acid by ignition.

SECTION IV.

VANADIUM.

Eq. 68·55 *or* 856·9; V.

Vanadium, so named from *Vanadis,* a Scandinavian deity, was discovered by Sefstrœm in 1830, in the iron prepared from the iron ore of Taberg, in Sweden, and procured afterwards in larger quantity from the slag of that ore. It was found afterwards by Mr. Johnston, in a new mineral discovered by him, the vanadiate of lead, from Wanlockhead. It is one of the rarest of the elements. The metal itself has considerable resemblance in properties to chromium. It combines with oxygen in three proportions, forming the protoxide of vanadium, VO, bioxide, VO_2, and vanadic acid, VO_3.

Protoxide of vanadium, VO, 76·55 *or* 956·9, is produced by the action of charcoal or hydrogen upon vanadic acid. It is a black powder of semi-metallic lustre, and when made coherent by pressure, conducts electricity like a metal. It does not combine with acids, and exhibits none of the characters of an alkaline base. It is readily oxidised when heated in the open air, and passes into the following compound.

Bioxide of vanadium, Vanadic oxide, VO_2, 84·55 *or* 1056·9, is produced by the action of hydrosulphuric acid and other deoxidating substances upon vanadic acid. When pure, it is a black pulverulent substance, quite free from any acid or alkaline reaction. It dissolves in acids, and forms salts, most of which are of a blue colour. Vanadic salts form, with the *hydrates* and *monocarbonates* of the *fixed alkalies,* a greyish-white precipitate of hydrated vanadic oxide, which dissolves in a moderate excess of the reagent, but is precipitated by a large excess in the form of a vanadite of the alkali. *Ammonia* in excess produces a brown precipitate, soluble in pure water, but insoluble in water containing ammonia. *Ferrocyanide of potassium* forms a yellow precipitate, which turns green on exposure to the air. *Hydrosulphuric acid* produces no precipitate. *Sulphide of ammonium* forms a black-brown precipitate, soluble in excess. *Tincture of galls* forms a finely-divided black precipitate, which gives to the liquid the appearance of ink.

Bioxide of vanadium is also capable of acting as an acid, and forms compounds with alkaline bases, some of which are crystallisable. It is hence called *vanadous acid,* and its salts *vanadites.* These salts in the dry state are brown or black; they are all insoluble in water, excepting those of the alkalies. The solutions of the alkaline vanadites are brown, but when treated with hydrosulphuric acid, they acquire a splendid red-purple colour, arising from the formation of a sulphur-salt. Acids colour them blue, by forming a double salt of vanadic oxide and the alkali. Tincture of galls colours them blackish-blue. The insoluble vanadites, when moistened or covered with water, become green, and are converted into salts of vanadic acid.

Vanadic acid, VO_3; 92·55 *or* 1156·9.—It is in this state that vanadium occurs in the slag of the iron-ore of Taberg, and in the vanadiate of lead. It is obtained by dissolving the latter mineral in nitric acid, and precipitating the lead and arsenic, with which the vanadium is accompanied, by hydrosulphuric acid. A blue solution of bioxide of vanadium remains, which becomes vanadic acid when evaporated to dryness. Vanadic acid fuses but retains its oxygen at a strong red heat. It is very sparingly soluble, water taking up only 1-100th of its weight of this compound, thereby acquiring a yellow colour and an acid reaction. It acts the part of a base to stronger acids. An interesting double phosphate of silica and vanadic acid was observed in crystalline scales, of which the formula is $2SiO_3.PO_5+2VO_3.PO_5+6HO$. Vanadic acid forms, with bases, neutral and acid salts, the first of which admit of an isomeric modification, being both white and yellow, while the acid salts are of a fine orange-red. Vanadic and chromic acids are the only acids of which the solution is red, while they are distinguished from each other by the vanadic acid becoming blue, and the chromic acid green, when they are deoxidised. All the vanadiates are, more or less soluble in water; some of them, however, as the baryta and lead salts, are very sparingly soluble. The vanadiates of the alkalies are sparingly soluble in cold water, especially if it contains a free alkali or another alkaline salt; *e. g.*, vanadiate of ammonia is nearly insoluble in water containing sal-ammoniac; hence on treating a solution of vanadiate of potash with excess of sal-ammoniac, a precipitate of vanadiate of ammonia is produced. The aqueous solutions of the vanadiates are coloured red by the stronger acids, but the mixture often becomes colourless again after a while. They give orange-red precipitates with the salts of *teroxide of antimony, protoxide of lead, protoxide of copper,* and *protoxide of mercury. Hydrosulphuric acid* produces in neutral solutions of the vanadiates a mixed precipitate of sulphur and hydrated vanadic oxide; in acid solutions, it merely throws down sulphur and reduces the vanadic acid to vanadic oxide. *Sulphide of ammonium* imparts to solutions of the vanadiates a brown-red colour, and, on adding an acid to the solution, a light brown precipitate is formed, consisting of vanadic sulphide mixed with sulphur; the liquid at the same time generally acquires a blue colour.

All compounds of vanadium heated with *borax* or *phosphorus salt* in the outer blowpipe flame, produce a clear bead, which is colourless if the quantity of vanadium be small, yellow if it be large; in the inner flame, the bead acquires a beautiful green colour.

Sulphides and chlorides of vanadium, corresponding with the bioxide and vanadic acid have likewise been formed.*

ESTIMATION OF VANADIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Vanadium, in the state of vanadic oxide or vanadic acid, is estimated by reducing it to the state of protoxide by ignition in a stream of hydrogen; 100 parts of the protoxide contain 90·54 of the metal.

In solutions of vanadous salts, the vanadium is precipitated by mixing the solution with excess of mercuric chloride (corrosive sublimate), and then with ammonia. The precipitate, consisting of mercuric vanadiate, and amido-chloride of mercury, is ignited, whereupon vanadic acid remains mixed only with a small quantity of mercuric oxide, from which it is separated by solution in carbonate of ammonia.

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* Berzelius, Ann. Ch. Phys. [2.] xlvii. 337.

When vanadic acid is dissolved in a liquid, it may be obtained by evaporating the liquid, and if volatile acids or ammonia are also present, by igniting the residue.

Vanadic acid may be separated from many acids and other substances, by causing it to unite with ammonia, expelling the excess of ammonia by evaporation, and then adding a saturated solution of sal-ammoniac, in which vanadiate of ammonia is insoluble. The precipitate is then washed on a filter, first with solution of sal-ammoniac, then with alcohol, and the ammonia driven off by ignition. This method serves to separate vanadic acid from the fixed alkalies.

Vanadium may be separated from many of the preceding metals by the solubility of its sulphide in sulphide of ammonium; and from others, which are precipitated from their acid solutions by hydrosulphuric acid, by acidulating the liquid, and passing hydrosulphuric acid gas through it; the vanadium then remains dissolved in the form of vanadic oxide.

From *lead*, *baryta*, and *strontia*, vanadic acid may be separated by fusion with bisulphate of potash; on treating the fused mass with water, sulphate of lead, baryta, or strontia remains, while vanadiate of potash is dissolved. Sulphuric acid cannot be used to effect this separation, because the precipitated sulphate always carries down with it a portion of the vanadium.

SECTION V.

TUNGSTEN.

Syn. WOLFRAM. *Eq.* 94·64, *or* 1183; W.

This element exists in the form of tungstic acid in several minerals, the most important of which are the native *tungstate of lime* $CaO.WO_3$, and *wolfram*, or the tungstate of manganese and iron, $MnO.WO_3 + 3(FeO.WO_3)$. Its name tungsten means in Swedish, *heavy stone,* and is expressive of the great density of its compounds.

Tungstic acid parts with oxygen easily, and may be reduced in a glass tube, by means of dry hydrogen gas, at a red heat. The metal is thus obtained in the state of a dense, dark grey powder, which it is necessary to expose to a very violent heat to fuse into globules, for tungsten is even less fusible than manganese. The metal, when fused, has the colour and lustre of iron, and is not altered in air: it is one of the densest of the metals, its specific gravity being from 17·22 to 17·6. By passing the vapour of chloride or oxychloride of tungsten mixed with hydrogen, through a red-hot glass tube, the metal is obtained in the form of a dense specular film of steel-grey colour, and sp. gr. 16·54 (Wöhler). When heated to redness in the pulverulent form, it takes fire, burns, and is converted into tungstic acid. Tungsten forms two compounds with oxygen, viz., tungstic oxide, WO_2, and tungstic acid, WO_3.

Tungstic oxide, WO_2, 110·64 or 1383.—This oxide is obtained as a brown powder when tungstic acid is reduced by hydrogen at a temperature not exceeding low redness. Tungstic acid may also be deprived of oxygen in the humid way, by pouring diluted hydrochloric acid over it, and placing zinc in the liquor; the tungstic acid then gradually changes into tungstic oxide, in the form of brilliant crystalline plates of a copper-red colour. No saline compounds of this oxide with acids are known. When digested in a strong solution of hydrate of potash, it dissolves, with disengagement of hydrogen gas and formation of tungstate of potash.

A compound of tungstic oxide and soda, $NaO.2WO_2$, of a very singular nature, was discovered by Wöhler. It is obtained by adding to fused tungstate of soda as much tungstic acid as it will take up, and exposing the mass at a red heat to hydrogen gas. After dissolving out the neutral undecomposed tungstate by water, the new compound remains in golden yellow scales and regular cubes, possessing the metallic lustre of, and a striking resemblance to gold. This compound is not decomposed by aqua regia, sulphuric or nitric acid, or by alkaline solutions, but yields to hydrofluoric acid. It cannot be prepared by uniting soda directly with tungstic oxide.

Tungstic acid, WO_3; 118·64 or 1483, is most conveniently obtained by decomposing the native tungstate of lime, finely pulverised, by hydrochloric acid; chloride of calcium is dissolved, and tungstic acid precipitates. It is also obtained from wolfram by digesting that mineral in nitro-hydrochloric acid, which dissolves the oxides of iron and manganese, and leaves the tungstic acid in the form of a yellow powder—or by fusing the mineral with four times its weight of nitre; treating the fused mass with water to dissolve out the tungstate of potash thereby produced; adding chloride of calcium to the filtrate to throw down the tungstic acid as tungstate of lime; and decomposing the washed lime-salt with nitric acid. Dissolved in ammonia and reprecipitated by acids, tungstic acid always forms a compound with the acid employed. It may be obtained in the separate state by heating the tungstate of ammonia to redness. It is an orange-yellow powder, which becomes dull green when strongly heated. Its density is 6·12. It is quite insoluble in water and in acids, but dissolves in alkaline solutions.

Tungstic acid forms both neutral and acid salts with the alkalies. Neutral *tungstate of potash* $KO.WO_3$ is a very soluble salt, which may be obtained in small crystals by evaporating its solution. When a little acid is added to the solution, an acid salt precipitates, which is very slightly soluble in water. The neutral *tungstate of soda* is also very soluble, but may be obtained in good crystals, which contain a large quantity of water of crystallisation. The acid tungstate of soda $NaO.2WO_3$ is very crystallisable, and soluble in eight parts of water. A combination of tungstic acid with tungstic oxide, $WO_2.WO_3$, is obtained as a fine blue powder when tungstate of ammonia is heated to redness in a retort, and is also produced under other circumstances. Malaguti is disposed to consider this compound as a distinct acid of tungsten, W_2O_5.*

All the salts of tungstic acid have a very high specific gravity. The alkaline and earthy tungstates are colourless. The only soluble tungstates are those of the alkalies and magnesia. Solutions of the alkaline tungstates give, with hydrochloric, nitric, sulphuric, and phosphoric acid, white precipitates consisting of compounds of tungstic acid with the other acid. The precipitate formed by phosphoric acid dissolves in excess of that reagent; the precipitates formed by the other three acids turn yellow on boiling. A solution of an alkaline tungstate supersaturated with sulphuric, hydrochloric, phosphoric, oxalic, or acetic acid, yields, on the introduction of a piece of zinc, a beautiful blue colour arising from the formation of blue oxide of tungsten; this effect is not produced with nitric, tartaric, or citric acid. Solutions of alkaline tungstates form with lime-water and with salts of baryta, lime, zinc, lead, mercury, and silver, white precipitates consisting of tungstates of those bases. A soluble tungstate mixed with sulphide of ammonium and then with an acid in excess, yields a light brown precipitate of sulphide of tungsten, soluble in sulphide of ammonium.

With borax and phosphorus-salt in the outer blow-pipe flame, tungstic acid forms a colourless bead; in the inner flame it forms with borax, a yellow glass, if the quantity of tungsten present be somewhat considerable, but colourless with a smaller quantity. With phosphorus-salt in the inner flame it forms a glass of a pure blue colour, unless iron is also present, in which case the colour is blood-red; the addition of tin, however, renders it blue.

The above mentioned characters of tungstic acid, though general, are not invariable. Tungstic acid appears to be susceptible of certain modifications analogous to those of phosphoric acid, and depending upon the proportions in which it unites with water and other bases. In some of these modifications it is much more soluble than in others, and is not precipitated by nitric or hydrochloric acid.

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* Ann. Ch. Phys. [2], lx. 271.

Laurent distinguished five or six classes of tungstates, viz.,

1. *Ordinary tungstates*, WO_3MO, with or without water (M denoting a metal or hydrogen). To this class belong the neutral potash, soda, and baryta-salts, and most of the insoluble salts of tungstic acid. No acid salts of this class appear to exist. The solution of an ordinary tungstate dropped into excess of dilute nitric acid produces a gelatinous precipitate. The hydrated tungstic acid obtained by the action of aqua regia on wolfram belongs to this variety, its formula being $WO_3.HO$. 2. *Paratungstates*, $W_4O_{12}.2MO$, with or without water. To this class belong the salts commonly called bitungstates of potash, soda, ammonia, baryta, &c. They all, excepting the soda-salt, dissolve but sparingly in water. The solutions give no precipitate on the addition of very small quantities of nitric acid, or of very weak hydrochloric acid. They give precipitates with the ammoniacal solutions of nitrate of magnesia, zinc, and silver, which the ordinary tungstates do not. 3. *Metatungstates*, $W_3O_9.MO$, with or without water. The ammonia-salt of this variety is formed by boiling a solution of the paratungstate for several hours; the solution filtered when cold and then evaporated to a syrup, yields very soluble octohedrons. The solution is not precipitated by concentrated hydrochloric acid.—4. *Isotungstates*, $W_2O_6.MO$, with or without water. The ammonia-salt is formed by boiling metatungstate of ammonia with excess of ammonia; it is but slightly soluble in water. The acid, which may be separated from it by means of another acid, is principally characterised by reproducing the isotungstate when treated with ammonia. 5. *Polytungstates*, $W_6O_{18}.3MO$. When the yellow acid obtained from wolfram is treated with ammonia, and the solution slowly evaporated, paratungstate of ammonia is first deposited and afterwards the isotungstate. The mother-liquor separates

into two layers, one of which is brown and syrupy, and changes on drying to an easily soluble crystalline mass, probably a double salt of ammonia and iron. Boiled with strong nitric acid, it yields a precipitate which is not gelatinous, and does not turn yellow when boiled. Polystungstic acid is further characterised by forming with ammonia a very soluble salt, which becomes gummy on evaporation. 6. Laurent also, mentioned another class of tungstates, viz., *Homotungstates,* containing $W_5O_{15}.MO$. According to Margueritte * also there exist acid tungstates containing 3, 4, 5 and 6 eq. of acid to 1 eq. of base.

The composition of the tungstates has also been recently examined by W. Lotz †, whose results differ in many points from the preceding. According to Lotz, crude tungstic acid, obtained from wolfram by the action of hydrochloric and a small quantity of nitric acid, yields by digestion with ammonia and evaporation at a very gentle heat, yellow needles of an ammonia-salt containing $3NH_4O.7WO_3 + 6HO$, or $2(NH_4O.2WO_3) + NH_4O.3WO_3 + 6HO$. By mixing warm concentrated solutions of 1 eq. of monotungstate of soda, and rather more than 1 eq. chloride of ammonium, a double salt is obtained, composed of $(2NH_4O.WO_3) + NaO.WO_3 + 3HO$; and by adding 1 eq. metatungstate of soda to a boiling solution of 2 eq. chloride of ammonium, another double salt is formed containing $3NaO.7WO_3 + 4(3NH_4O.7WO_3) + 14HO$. The needle-shaped ammonia-salt mixed with solutions of the neutral salts of barium, strontium, manganese, nickel, and lead, yields precipitates of the general formula $3MO.7WO_3$. With alumina a white curdy precipitate is formed containing $Al_2O_3.7WO_3 + 9HO$. Sesquioxide of chromium forms a salt of a similar constitution. With magnesia, a sparingly soluble crystalline double salt is formed, containing $2(MgO.2WO_3) + NH_4O.3WO_3 + 10HO$; a similar double salt with zinc. Cadmium also forms a double salt containing $3NH_4O \cdot 7WO_3 + 4(3CdO \cdot 7W_3O) + 35HO$. To the octohedral tungstate of ammonia, which was regarded by Margueritte as $NH_4O \cdot 3WO_3 + 5HO$, and by Laurent as a metastungstate containing $(NH_4)_{\frac{5}{3}}H_{\frac{1}{3}}W_3O_{10} + 5HO$, or $\left.\begin{matrix}5NH_4O\\HO\end{matrix}\right\}$ $18WO_3 + 30HO$. Lotz assigns the formula $2(NH_4O \cdot 4WO_3) + 15$ eq. The solution of this salt is not precipitated by nitric or hydrochloric acid at ordinary temperatures, but after continued boiling yields a yellow precipitate; but if it be previously mixed with potash, the addition of an acid produces an immediate white precipitate, which turns yellow on boiling; the needle-shaped salt gives an immediate precipitate with acids, without previous addition of alkali. The octohedral salt differs from the needle-shaped salt also, in not forming precipitates with solutions of the earths and other metallic oxides, except when previously mixed with ammonia, by which, indeed, it is converted into the salt $3NH_4O \cdot 7WO_3$.

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* Ann. Ch. Phys. [3], xvii. 475.

† Ann. Ch. Pharm. xci. 49.

Sulphides of tungsten.—The bisulphide is prepared by mixing one part of tungsten with six parts of cinnabar, and exposing the mixture, covered with charcoal, in a crucible, to a white heat; or, according to Roche, by fusing bitungstate of potash with an equal weight of sulphur, and washing the fused mass with water. The tersulphide is formed by dissolving tungstic acid in an alkaline sulphide, and precipitating by an acid. It is of a liver-brown colour, and becomes black on drying. The tersulphide of tungsten has a certain degree of solubility in water containing no saline matter, and is a strong sulphur-acid. The salt $KS.WS_3$ forms pale red crystals. Two parts of this sulphur-salt dissolved in water with one part of nitre, give large and beautiful ruby-red crystals of a double salt, $KS.WS_3 + KO.NO_5$.

Phosphides of tungsten.—Phosphorus and tungsten combine directly, but without emission of light and heat, when finely pounded metallic tungsten contained in a glass tube is heated to redness in phosphorus vapour. The resulting compound is a dull, dark grey powder, very difficult to oxidise, and containing W_3P_2. Another compound, W_4P, is obtained in magnificent crystalline groups, having exactly the appearance of natural geodes, by reducing a mixture of 2 eq. phosphoric and 1 eq. tungstic acids at a very high temperature in a crucible lined with charcoal. The crystals are six-sided prisms, sometimes an inch long, of a steel-grey colour, and strong lustre; their specific gravity is 5·207. This compound is a perfect conductor of electricity; undergoes no change when heated to the melting point of manganese in a close vessel, and remains nearly unaltered when heated to redness in the air; but burns with great splendour on charcoal in a stream of oxygen, or on fused chlorate of potash; it is not attacked by any acid, not even by aqua-regia (Wöhler).*

Bichloride of tungsten, WCl_2, is formed when metallic tungsten is heated in chlorine gas. It condenses in dark red needles, which are very fusible and volatile. This chloride is decomposed by water, and tungstic oxide with hydrochloric acid formed.

Terchloride of tungsten, WCl_3, is produced at the same time as the last compound, and also when the sulphide of tungsten is heated in chlorine gas. It forms a sublimate of beautiful red crystals, which are resolved by water into tungstic and hydrochloric acids. A *chlorotungstic acid*, or double compound of terchloride of tungsten and tungstic acid, WO_2Cl, or $WCl_3 . 2WO_3$, is prepared by heating tungstic oxide in chlorine gas. It condenses in yellow crystalline scales: when suddenly heated, it is resolved into tungstic acid, bichloride of tungsten, and chlorine. Another compound is known, containing $2WCl_3 . WO_3$ (Bonnet).

According to A. Riche†, the terchloride of tungsten is the only product obtained when tungsten is heated in pure dry chlorine gas: it crystallises in needles, not of a red but of a steel-grey colour. The bichloride is formed in small quantity, as a blackish-brown mass, by heating the terchloride in dry hydrogen; and the red oxychloride WCl_2O, by passing chlorine gas over a mixture of tungstic acid and charcoal, and distilling the product in an atmosphere of hydrogen.

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* Chem. Soc. Qu. J. v. 94.

† Compt. rend. xlii. 203.

ESTIMATION OF TUNGSTEN, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Tungsten is always estimated in the form of tungstic acid. When this acid exists in a solution not containing any other fixed substance, it is sufficient to evaporate to dryness and ignite the residue. The tungstic acid is then obtained in a state of purity, and contains 79·76 per cent. of the metal. Tungstic oxide is easily converted into tungstic acid by fusion with carbonate of soda.

The best method of separating tungstic acid from the *fixed alkalies* is to treat the solution, after exact neutralisation with nitric acid, with a solution of mercurous nitrate. Mercurous tungstate is then precipitated, and the mercury may be expelled from the dried precipitate by careful ignition in a good draught.

The separation of tungstic acid from the *earths* may be effected by decomposing the compound with nitric acid, and treating the decomposed mass with carbonate of ammonia, which dissolves the tungstic acid.

Tungstic acid may be readily separated from many metallic oxides, such as the oxides of *iron, manganese, nickel, cobalt, lead,* &c., by fusing the whole with carbonate of soda, and digesting the fused mass with water, which dissolves the tungstic acid and leaves the oxides undissolved.

From *titanic acid,* tungstic acid is separated by ammonia, which dissolves only the latter.

The best mode of separating tungstic acid from *chromic* *acid*, is to treat the concentrated solution with excess of hydrochloric acid, which precipitates the greater part of the tungstic acid; then boil with alcohol to reduce the chromic acid to chromic oxide; and dissolve the tungstic acid by ammonia.

SECTION VI.

MOLYBDENUM.

Eq. 47·88 *or* 598·5; Mo.

This metal is closely allied to tungsten. Its native sulphide was first distinguished from plumbago by Scheele, in 1778; and a few years afterwards, molybdic acid, which he had formed, was reduced, and molybdenum obtained from it, by another Swedish chemist, Hjelm. The name molybdenum is derived from the Greek term for plumbago.

The oxides of molybdenum are easily reduced, when exposed to a strong heat in a crucible lined with charcoal, but the metal itself is very refractory. Bucholz, who obtained it in rounded buttons, found it to be a white metal, of density between 8·615 and 8·636. It may be reduced from its chlorides by hydrogen, like tungsten (p. 177.), and then forms a light steel-grey specular deposit, adhering to the glass (Wöhler). It is not acted upon by hydrochloric, hydrofluoric, or diluted sulphuric acid; but is dissolved by concentrated sulphuric acid, by nitric acid, and by aqua-regia. Hydrate of potash does not dissolve this metal in the humid way. Molybdenum combines in three proportions with oxygen, forming molybdous oxide, MoO, molybdic oxide, MoO_2, and molybdic acid, MoO_3.

Molybdous oxide, MoO, 55·88 *or* 698·5.—This oxide is obtained by adding to the concentrated solution of any molybdate, so much hydrochloric acid as to redissolve the molybdic acid which is at first thrown down, and placing zinc in the liquid; this becomes first blue, then reddish-brown, and finally black, and contains the chloride of zinc and protochloride of molybdenum. To separate the oxide of molybdenum from the oxide of zinc, ammonia is added to the liquid in quantity no more than sufficient to precipitate the former, while the latter remains in solution. The molybdous oxide carries down with it a portion of oxide of zinc, from which it may be freed by washing with ammonia: it is thus obtained as a hydrate of a black colour. The hydrate of molybdous oxide dissolves with difficulty in acids, forming solutions which are almost black and opaque, and which do not yield crystallisable salts. These solutions yield with the *alkalies* and their *carbonates* a brownish-black precipitate of the hydrated oxide, insoluble in the caustic alkalies, slightly soluble in the neutral carbonates, but readily soluble in bicarbonate of potash or carbonate of ammonia. *Hydrosulphuric acid* throws down a brown-black precipitate, and *sulphide of ammonium* a yellowish-brown precipitate of sulphide of molybdenum, easily soluble in sulphide of ammonium. *Ferrocyanide* or *ferricyanide* of potassium forms a dark-brown precipitate, insoluble in excess. *Phosphate of soda* forms a brownish-white precipitate. Molybdous oxide resists, after ignition, the action of all acids.

Molybdic oxide, MoO_2; 63·88 *or* 798·5.—This oxide may be obtained by igniting molybdate of ammonia in a covered crucible, but mixed with a little molybdic acid. It is better procured by igniting rapidly, in a covered crucible, a mixture of anhydrous molybdate of soda (which may contain an excess of soda) with sal-ammoniac. Water poured upon the fused mass dissolves common salt, and leaves a brown powder almost black. But molybdic oxide prepared in this way is insoluble in acids. The hydrated oxide may be obtained in various ways, one of which consists in digesting molybdic acid with hydrochloric acid and copper, till all the molybdic acid is dissolved. From the solution, which is of a deep-red colour, molybdic oxide is precipitated, in appearance exactly similar to the hydrated sesquioxide of iron, by ammonia added in sufficient excess to retain all the oxide of copper in solution. The hydrate has a certain degree of solubility in pure water, and should, therefore, be washed with solution of sal-ammoniac, and lastly with alcohol. This hydrate reddens litmus paper, but possesses no other property of an acid. It is not dissolved by the hydrated alkalies, but is soluble in their carbonates, like several earths and metallic oxides. It dissolves in acids and forms salts, which are red when they contain water of crystallisation, and black when anhydrous. The aqueous solutions of these salts have a reddish-brown colour, and a rough, somewhat acid and subsequently metallic taste. When heated in the air, they have a tendency to become blue by oxidation. With *zinc*, they first blacken, and then yield a black precipitate of hydrated molybdous oxide. Their behaviour with alkalies, hydrosulphuric acid &c., is similar to that of the molybdous salts, excepting that the precipitates are lighter in colour. The oxalate of molybdic oxide may be obtained in crystals by spontaneous evaporation.

Molybdic acid, MoO_3; 71·88 *or* 898·5.—The native sulphide of molybdenum, in fine powder, is roasted in an open crucible, with constant stirring, at a heat not exceeding low redness, so long as sulphurous acid goes off. It leaves a dull yellow powder, which is impure molybdic acid. This is dissolved in ammonia, and the molybdate of ammonia purified by evaporation, during which some foreign matters are deposited, and crystallised. The crystallised salt, exposed to a moderate heat, so as to avoid fusion, gives off its ammonia, and leaves molybdic acid in a state of purity. The acid thus prepared is a white and light porous mass, which may be diffused in water, and divides into little crystalline scales of a silky lustre. It fuses at a red heat, and forms on cooling a straw-coloured crystalline mass, the density of which is 3·49. This acid forms no hydrate. It requires 570 times its weight of water to dissolve it. Before being ignited, it is soluble in acids, and forms a class of compounds, in which it appears to play the part of base, but of which not much is known. When boiled with bitartrate of potash, molybdic acid dissolves, even after being fused by heat.

When a solution of bichloride of molybdenum is poured into a saturated or nearly saturated solution of molybdate of ammonia, a blue precipitate falls, which is a *molybdate of molybdic oxide*, $MO_2.2MO_3$. This compound is likewise readily formed in a variety of other circumstances.

The salts of molybdic acid are colourless, when their base is not coloured. When they are treated with other acids, molybdic acid is precipitated, but dissolves in an excess of the acid. It forms both neutral and acid salts with the alkalies. These alkaline molybdates are the only ones that are easily soluble in water; of the rest, some dissolve sparingly, and others are completely insoluble. Solutions of the alkaline molybdates are coloured yellow by *hydrosulphuric acid* from formation of a sulphomolybdate of the alkali-metal (MS,MoS_3), and then yield with acids a brown precipitate of tersulphide of molybdenum. This is an extremely delicate test for molybdic acid. They form white precipitates with salts of the *earths*, and precipitates of various colours with salts of the heavy metals; *e. g.* white with *lead* and *silver* salts; yellow with *ferric* salts; and yellowish-white with *mercurous* salts.—*Protochloride of tin* produces immediately a greenish blue precipitate, soluble in hydrochloric acid forming a green solution; which turns blue on the addition of a very small quantity of the tin-solution.—When *tribasic phosphoric acid*, or a liquid containing it, is added to the solution of molybdate of ammonia, together with an excess of hydrochloric acid, the liquid turns yellow, and after a while deposits a yellow precipitate of molybdic acid combined with small quantities of phosphoric acid and ammonia. This precipitate is soluble in ammonia and likewise in excess of the phosphate. The reaction is therefore especially adapted for the detection of small quantities of phosphoric acid. The bibasic and monobasic phosphates do not produce the yellow precipitate. *Arsenic acid* gives a similar reaction. According to Seligsohn*, the yellow precipitate is a *phosphomolybdate of ammonia* $2(3NH_4O\,.\,PO_5) + 15(HO\,.\,4MoO_3)$. By digesting it in a dilute solution of acetate of potash or soda, crystalline double salts are formed, containing $2(3NH_4O.PO_5) + 15\left(\left.\begin{matrix}KO\\ \text{or }NaO\end{matrix}\right\}.4MoO_3\right)$. With acetate of baryta, a double salt is formed, containing $3NH_4O.PO_5 + 30(BaO.MoO_3)$; and similarly with acetate of lead.

Molybdic acid and other compounds of molybdenum form a colourless bead with *borax* and *phosphorus-salt* in the outer blowpipe flame. In the inner flame, they form a brown bead with borax and a green bead with phosphorus-salt.

Molybdates of potash.—The *monomolybdate*, $KO.MoO_3$, is obtained by agitating the termolybdate with an alcoholic solution of potash: it then separates as an oily mass, which, when dried over lime and sulphuric acid, crystallises in four-sided prisms containing $2(KO.MoO_3) + HO$. It is also obtained by mixing a solution of molybdate of ammonia with excess of carbonate of potash, and evaporating to a syrup. Bimolybdate of potash does not appear to exist. When a solution of molybdic acid in carbonate of potash is mixed with strong nitric or hydrochloric acid till a slight permanent precipitate is produced, the liquid after a while yields crystals of a salt containing $4KO.9MoO_3 + 6HO$: and this salt is decomposed by water into monomolybdate, which dissolves readily, and termolybdate which is sparingly soluble:

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* J. pr. Chem. lxvii. 474.

$$2(4KO.9MoO_3) = 3(KO.MoO_3) + 5(KO.3MoO_3).$$

The *termolybdate* dissolves easily in boiling water, and separates as a bulky white precipitate when the solution is quickly cooled; but by slow cooling it is obtained in needles, having a beautiful silky lustre and containing $KO.3MoO_3 + 3\ HO$. Nitric acid added in excess to a solution of molybdic acid in carbonate of potash throws down a white precipitate consisting sometimes of *quadromolybdate* and sometimes of *pentamolybdate* of potash, both anhydrous (Svanberg and Struve).*

Monomolybdate of soda, $NaO.MoO_3 + 2HO$, is obtained by fusing molybdic acid with an equivalent quantity of carbonate of soda. It is easily soluble in water, and crystallises in small rhombohedrons, which melt easily and give off their water. The *bimolybdate,* $NaO.2MoO_3 + HO$, is obtained in a similar manner. It crystallises in needles, aud dissolves sparingly in cold, readily in boiling water. The *termolybdate* is obtained by adding nitric acid to a solution of molybdic acid in carbonate of soda, as a bulky white precipitate, more soluble than the corresponding potash-salt. The solution yields crystals containing $NaO.3MoO_3 + 7HO$. Nitric acid added in excess to a solution of molybdate of soda throws down nothing but molybdic acid (Svanberg and Struve).†

Monomolybdate of ammonia, $NH_4O.MoO_3$, obtained by treating molybdic acid in excess with strong solution of ammonia in a closed vessel, then precipitating with alcohol, and drying over quick lime, forms microscopic four-sided prisms, which are anhydrous. The *bimolybdate,* $NH_4O.2MoO_3$, is deposited as a white crystalline powder when a solution of molybdic acid in excess of ammonia is quickly evaporated. A solution of molybdic acid in ammonia, evaporated by heat to the crystallising point, or left to evaporate in the air, deposits large transparent six-sided prisms containing $NH_4O.2MoO_3 + NH_4O.3MoO_3 + 3HO$ (Svanberg and Struve).

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* Ann. Ch. Pharm. lxviii. 494.

† Ann. Ch. Pharm. lxviii. 404.

Monomolybdate of baryta, $BaO.MoO_3$, is precipitated as a sparingly soluble crystalline powder on adding chloride of barium to a solution of molybdic acid in excess of ammonia. Baryta-salts, containing $BaO.3MoO_3 + 3HO$ and $BaO.2MoO_3 + BaO_2 3MoO_3 + 6HO$, are obtained by precipitating the corresponding potash and ammonia-salts with chloride of barium. By decomposing monomolybdate of baryta with dilute nitric acid, an acid salt is formed containing $BaO.9MoO_3 + 4HO$; it crystallises in small six-sided prisms, fusible and insoluble in water (Svanberg and Struve).

Monomolybdate of magnesia, $MgO.MoO_3 + 5HO$, is obtained in distinct crystals by boiling molybdic acid and *magnesia alba* with water, and evaporating the filtrate; it gives off 3 eq. water at 212° (Struve).*

Molybdate of manganous oxide, $MnO.MoO_3 + HO$, is obtained as a heavy white powder, by treating carbonate of manganese with termolybdate of potash or soda.

Protosulphate of iron added to a solution of molybdate of potash, reduces the molybdic acid to a lower state of oxidation; but if chlorine gas be passed through the solution at the same time, a bulky precipitate is formed, which, when dried in the air, forms a light yellow powder, consisting of *pentamolybdate of ferric oxide*, $Fe_2O_3.5MoO_3 + 16HO$.

By boiling the solution of termolybdate of potash or soda, or acid molybdate of ammonia, with hydrate of *alumina, manganic oxide, ferric oxide*, or *chromic oxide*, and evaporating to the crystallising point, double salts are obtained. The composition of the double salts containing alumina, ferric oxide, or chromic oxide with potash or oxide of ammonium, may be represented by that of the alumina and potash-salt, viz.,

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* Ann. Ch. Pharm. xcvi. 266.

$Al_2O_3.6MoO_3 + 3(KO.2MoO_3) + 20HO$. The *potassio-manganic* salt contains $Mn_2O_3.6MoO_3 + 5(KO.2MoO_3) + 12HO$. The *ammonio-manganic* salt is similarly constituted. The *sodio-chromic* salt contains $Cr_2O_3.6MoO_3 + 3(NaO.2MoO_3) + 21HO$ (Struve).

Acid molybdate of ammonia, added to a boiling solution of sulphate of copper, throws down a heavy green amorphous powder, consisting of *basic molybdate of copper,* $4CuO.3MoO_3 + 5HO$. By adding molybdate of ammonia in excess to a cold solution of sulphate of copper, a double salt is formed, consisting of $CuO.2MoO_3 + NH_4O.3MoO_3 + 9HO$. It is a white-blue crystalline powder, which gives off 4 eq. of water at 212° and 4 eq. more at 266° (Struve).

Molybdate of lead, $PbO.MoO_3$, is formed by precipitating nitrate of lead with termolybdate of potash. It is a heavy white powder which melts only at a high temperature. It occurs finely crystallised as a mineral. Chromate of lead is dimorphous, and corresponds in the least usual of its forms with molybdate of lead: hence molybdenum is connected with the magnesian metals, and tungsten also with the same class, from the isomorphism of the tungstates and molybdates.

Sulphides of molybdenum.—The *bisulphide* is the ore from which the compounds of this metal are derived. It occurs in many parts of Sweden, and might be procured in quantity if any useful application of the metal were discovered. It is a lead-grey mineral, having the metallic lustre, composed of flexible laminæ, soft to the touch, and making a streak upon paper like plumbago. Nitric acid oxidates it easily, without dissolving it. Its density is from 4·138 to 4·569. A *tersulphide of molybdenum* is obtained in the same way as the corresponding compound of tungsten, and affords crystallisable sulphur-salts which are red. The sulphomolybdate of potassium combines likewise with nitrate of potash. When a solution of the former salt is boiled with tersulphide of molybdenum in excess, the latter is converted into bisulphide of molybdenum, and a *quadrisulphide of molybdenum* dissolves in combination with the sulphide of potassium. The quadrisulphide may be precipitated by hydrochloric acid, and when dried is a cinnamon-brown powder.

Chlorides of molybdenum.—A *protochloride* is formed when molybdous oxide is dissolved in hydrochloric acid; the *bichloride* when molybdenum is heated dry in chlorine gas, as a dark-red gas which condenses in crystals, like those of iodine. It forms a crystallisable double salt with sal-ammoniac. *Chloromolybdic acid*, or a compound of terchloride of molybdenum and molybdic acid, MoO_2Cl, or $MoCl_3+2MoO_3$, is formed with (molybdic acid), when molybdic oxide is exposed to chlorine gas at a red heat. It sublimes below a red heat, and condenses in crystalline scales, which are white with a shade of yellow.

ESTIMATION OF MOLYBDENUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

The determination of molybdic acid is more difficult than that of tungstic acid, on account of its partial volatility. The best mode of estimating it is to convert it into molybdic oxide by ignition in an atmosphere of hydrogen; the oxide which is perfectly fixed may then be weighed; it contains 74·95 per cent. of the metal. When molybdic acid exists in solution in ammonia or in other acids, the solution must be carefully evaporated to dryness, and the residue treated as above.

Molybdic acid is separated from most metallic oxides by its solubility in sulphide of ammonium. The filtered solution is then treated with an excess of very dilute nitric acid, to precipitate the tersulphide of molybdenum; the precipitate collected on a weighed filter, and its quantity determined; after which, a weighed quantity of it is ignited in an atmosphere of hydrogen, to convert it into the bisulphide, MoS_2, from the weight of which the amount of molybdenum is calculated.

Molybdic acid is separated from the *earths* by fusing with carbonate of soda, and digesting the fused mass in water, which dissolves molybdate of soda, and leaves the earth in the form of carbonate.

From the *fixed alkalies*, molybdic acid may be separated by precipitation with mercurous nitrate, and its quantity estimated from the weight of the precipitate.

SECTION VII.

TELLURIUM.

Eq. 64·14 *or* 801·8; Te.

Tellurium is a metal of rare occurrence, and appeared at one time to be almost confined to certain gold mines in Transylvania; but it has been found lately, in considerable abundance, at Schemnitz, in Hungary, combined with bismuth; and in the silver mine of Sadovinski in the Altai, united with silver and with lead. It was first described as a new metal by Klaproth, who gave it the name of tellurium, from *tellus*, the earth.

Tellurium is chiefly obtained from telluride of bismuth. The ore, after being freed from the matrix by pounding and washing, is mixed with an equal weight of carbonate of potash or soda, the mixture made up into a paste with olive oil, and heated in a well closed crucible, carefully at first to prevent frothing, and afterwards to a full white heat. The fused mass is then digested in water; which leaves the bismuth and the excess of charcoal undissolved, and dissolves the tellurium in the form of telluride of potassium or sodium, which imparts a port-wine colour to the liquid. The solution deposits metallic tellurium when exposed to the air, or more quickly when air is blown through it; and the precipitated metal is purified by washing with acidulated water, and subsequent distillation in an atmosphere of hydrogen (Berzelius). The metal is also obtained from the ore called *foliated tellurium,* which contains 13 per cent. of tellurium, and 63 per cent. of lead, together with copper, gold, antimony, and sulphur. The finely pounded mineral is freed from the sulphide of lead and antimony by repeated boiling with strong hydrochloric acid and washing with water; the residual telluride of gold treated with strong nitric acid; the tellurium-solution poured off from the gold and evaporated to dryness; the residue dissolved in hydrochloric acid; and the tellurium precipitated from the solution by sulphurous acid (Berthier).*

In a state of purity, tellurium is silver-white and very brilliant. It is very crystallisable, assuming a rhombohedral form, in which it is isomorphous with arsenic and antimony. It is brittle for a metal, and an indifferent conductor of heat and electricity. Its density is from 6·2324 to 6·2578, according to Berzelius. Tellurium is about as fusible as antimony, and may be distilled at a high temperature. It burns in air, at a high temperature, with a lively blue flame, green at the borders, and diffuses a dense white smoke, which generally has the odour of decaying horse-radish, from the presence of a little selenium. Tellurium belongs to the sulphur-class of elements. Like selenium and sulphur, it dissolves to a small extent in concentrated sulphuric acid, and communicates to it a fine purple-red colour. In this solution, the metal is not oxidated, for it is precipitated again, in the metallic state, by water. This metal has also considerable analogy with antimony, and may probably connect together the sulphur and phosphorus families. Tellurium combines in two proportions with oxygen, forming tellurous acid, TeO_2, and telluric acid, TeO_3.

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* For further details respecting the extraction of tellurium, vide Berzelius, Traité de Chimie, i. 344; and the translation of Gmelin's Handbook, iv. 393. Wöhler states, in a note to his paper on telluride of ethyl (Ann. Ch. Pharm. lxxxiv. 70), that tellurium may be obtained in considerable quantities from the residues of the Transylvanian gold-extraction, which have hitherto been thrown away as worthless.

Tellurous acid, TeO_2; 80·14 *or* 1001·8.—This acid differs remarkably in properties according as it is anhydrous or hydrated.* Hydrated tellurous acid is obtained by precipitating bichloride of tellurium with cold water; or by fusing anhydrous tellurous acid with an equal weight of carbonate of potash, as long as carbonic acid is disengaged, dissolving the tellurite of potash in water, and adding nitric acid to it till the liquor distinctly reddens litmus paper. A white and bulky precipitate is produced, which is washed with ice-cold water, and afterwards dried without artificial heat. Tellurium likewise dissolves with violence in pure nitric acid of density 1·25, and if after the first five minutes, the clear liquid be poured into water, tellurous acid is precipitated in white flocks. But if not immediately precipitated, the nitric acid solution undergoes a change.

The hydrated acid obtained by these processes forms a light, white, earthy mass, of a bitter and metallic taste. It instantly reddens litmus paper, and while still moist, dissolves to a sensible extent in water. It is very soluble in acids, and the solutions are not subject to change, except that which is formed by nitric acid. Ammonia and the alkaline carbonates also dissolve hydrated tellurous acid with facility, the latter becoming bicarbonates.

Anhydrous tellurous acid.—When the solution of tellurous acid in water is heated to 140°, it deposits the anhydrous acid in grains, and loses its acid reaction. The same change occurs when an attempt is made to dry the hydrated tellurous acid by heat: it parts with combined water, and becomes granular. The solution of tellurous acid in nitric acid changes spontaneously in a few hours, and in a quarter of an hour when heat is applied to it, and allows the anhydrous acid to precipitate. When the deposition of the acid is slow, it forms a crystalline mass of fine grains, among which octohedral crystals may be perceived by the microscope. The acid is then anhydrous. In this state it does not redden litmus, or not till after a time. It is but very slightly soluble in water, and the solution has no acid reaction. At a low red heat, it fuses into a clear transparent liquid of a deep yellow colour, which on cooling becomes a white and highly crystalline mass, easily detached from a crucible. Tellurous acid is volatile, although less so than the metal itself.

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* Berzelius regarded the hydrated and anhydrous acids as containing different modifications of the same compound, and distinguished them as α-tellurous and β-tellurous acid.

The solutions of hydrated tellurous acid in the stronger acids yield a black precipitate of metallic tellurium, when treated with powerful deoxidising agents, such as zinc, phosphorus, protochloride of tin, sulphurous acid, and the alkaline bisulphates. Hydrosulphuric acid and sulphide of ammonium throw down black-brown sulphide of tellurium, easily soluble in excess of sulphide of ammonium.

The *tellurites*, or compounds of tellurous acid with salifiable bases, contain 1 atom of base united with 1, 2, or 4 atoms of acid. They are fusible, and generally solidify in the crystalline form on cooling; the quadrotellurites, however, form a glass. Tellurites are colourless unless they contain a coloured base; those which are soluble have a metallic taste. Most of them, when heated to redness with charcoal, yield metallic tellurium, sometimes with slight detonation; and the reduced metal volatilises readily, being at the same time reoxidised and forming a white deposit on the charcoal; it likewise imparts a green colour to the flame; the tellurites, when ignited with potassium, or with charcoal and carbonate of potash, yield telluride of potassium which dissolves in water, forming a port-wine coloured solution; with the zinc and silver-salts, however, and a few others, this reduction does not take place. The tellurites of ammonia, potash and soda are easily soluble in water; those of baryta, strontia, and lime are sparingly soluble; the rest, insoluble. An aqueous solution of a tellurite is decomposed by the carbonic acid of the air. Nearly all tellurites dissolve in strong hydrochloric acid without evolving chlorine when heated; the solution exhibits the above-mentioned characters of a solution of tellurous acid in the stronger acids, except in so far as it may be interfered with by the presence of another base. The solution when diluted in water yields a white precipitate of tellurous acid, provided the excess of hydrochloric acid present is not too great.

Monotellurite of potash, $KO.TeO_2$, is obtained by heating 1 eq. tellurous acid with eq. of carbonate of potash. The fused mass on cooling forms crystals of large size. The salt dissolves slowly in cold, more quickly in warm water. *Bitellurite of potash*, $KO.Te_2O_4$, is obtained by fusing two atoms of tellurous acid with one atom of carbonate of potash. It appears to be capable of existing in a hot solution, and of crystallising in certain circumstances; but it is decomposed by cold water, which resolves it into the neutral salt, which dissolves, and a *quadritellurite of potash*, $KO.Te_4O_8 + 4HO$. The latter salt cannot be redissolved in water, without decomposition. In losing its water when heated, it swells up like borax.

Telluric acid, TeO_3; 88·14 *or* 1101·8.—This acid is obtained in combination with potash, by fusing tellurous acid with nitre. It may then be transferred to baryta, and the insoluble tellurate of baryta decomposed by sulphuric acid. The solution of telluric acid gives bulky, hexagonal, prismatic crystals. Its taste is not acid, but metallic, resembling that of nitrate of silver. Indeed, it appears to be but a feeble acid, reddening litmus but slightly, when the solution is diluted. The crystallised acid contains 3HO, of which it loses 2HO by efflorescence, a little above 212°. It then appears insoluble in cold water, but may be completely redissolved by long digestion, particularly with ebullition, and is not permanently altered.

Anhydrous telluric acid.—The crystals of hydrated telluric acid give off all their water at a heat below redness, and are converted into a mass of a fine orange-yellow colour, without changing their form. This yellow matter, which is distinguished, as *alpha-telluric acid* by Berzelius, is remarkable for its indifference to chemical reagents, being completely insoluble in cold or boiling water, in hot hydrochloric and nitric acids, and in potash-ley. At a high temperature, it is decomposed, evolving oxygen, and leaving tellurous acid white and pulverulent.

Telluric acid has but slight affinity for bases. The hydrated acid withdraws from alkaline carbonates, only so much alkali as to form a biacid salt. Telluric acid forms bibasic, sesquibasic, monobasic, biacid, and quadracid salts. The tellurates are colourless, unless they contain a coloured base. At a red heat, they give off oxygen and are converted into tellurites. Before the blowpipe, they behave like the tellurites; also with reducing agents, such as protochloride of tin, and sulphurous acid, excepting that the reduction does not take place so quickly, and in some cases requires the application of heat. Hydrosulphuric acid, added to the solution of a tellurate, produces no change at first; but if the liquid be placed in a stoppered bottle and left for a while in a warm place, a brown precipitate of sulphide of tellurium is formed. Tellurates dissolve in cold strong hydrochloric acid without decomposition. The solutions are not yellow, like those of the tellurites in hydrochloric acid, and may be diluted with water without becoming milky, even though the excess of hydrochloric acid be but small. But on boiling the solution, chlorine is evolved, and the liquid, if subsequently mixed with water, gives a precipitate of tellurous acid, provided the excess of hydrochloric acid is not too great.

Neutral *tellurate of potash* is $KO.TeO_3 + 5HO$; the *bitellurate of potash*, $KO.Te_2O_6 + 4HO$; the *quadritellurate of potash*, $KO.Te_4O_{12} + 4HO$. All these salts may be obtained directly, in the humid way, by dissolving the proper proportions of hydrated acid and carbonate of potash together, in hot water. A portion of the combined water in the last two salts is unquestionably basic, but how much of it is so has not been determined. They cannot be made anhydrous by heat without being essentially altered in properties.

The neutral tellurate of potash undergoes no change in constitution under the influence of heat, resembling in that respect those tribasic phosphates of which the whole three atoms of base are fixed. The bitellurate of potash loses its water and becomes yellow at a temperature below redness, and is changed into a quadritellurate, which is insoluble both in water and in dilute acids. Water dissolves out neutral tellurate from the yellow mass. The insoluble salt is named, by Berzelius, the *alpha-quadritellurate* of potash. The elements of this compound are united by a powerful affinity. It is formed when hydrated telluric acid is intimately mixed with a potash-salt, such as nitre or chloride of potassium, and the mixture calcined at a temperature which should be much below a red heat; also when tellurous acid is ignited with chlorate of potash, and in other circumstances. Hydrate of potash dissolves the alpha-quadritellurate by fusion, and nitric acid by a long continued ebullition; but in both cases, the acid set free in the solution exhibits the properties of ordinary telluric acid.

Telluretted hydrogen, Hydrotelluric acid, TeH, is a gaseous compound of tellurium and hydrogen, analogous in constitution and properties to sulphuretted hydrogen. It is obtained by fusing tellurium with zinc or with tin, and acting on the mixture with hydrochloric acid.

Definite *sulphides of tellurium* have been obtained, corresponding with tellurous and telluric acids. They are sulphur-acids.

Two *chlorides of tellurium* have been formed, a protochloride, TeCl, to which there is no corresponding oxide, and a bichloride, $TeCl_2$. No higher chloride, corresponding with telluric acid, has been obtained.

Tellurium forms alloys with several metals, *e.g.*, with potassium, sodium, aluminum, bismuth, zinc, tin, lead, iron, copper, mercury, silver, and gold. Some of these alloys, as those of bismuth, silver, and gold, are found native.

Telluride of potassium is prepared by mixing 1 part of tellurium powder with 10 parts of burnt tartar; introducing the mixture into a porcelain retort fitted with a glass tube bent downwards at right angles; heating the retort to redness for three or four hours, as long, indeed, as carbonic oxide continues to escape; and then introducing the end of the bent tube into a flask kept full of carbonic acid gas, to prevent access of air; this latter precaution is necessary on account of the highly pyrophoric character of the product (Wöhler). The compound may also be obtained by heating tellurium with potassium, in a retort filled with hydrogen; combination then takes place attended with vivid combustion. Telluride of potassium dissolves in water, forming a port-wine coloured solution, which on exposure to the air becomes decolorised, and deposits tellurium in shining scales; with acids it evolves telluretted hydrogen gas. *Telluride of sodium* is prepared by similar methods, and possesses similar properties.

ESTIMATION OF TELLURIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

When tellurium exists in solution in the form of tellurous acid it is reduced to the metallic state by sulphurous acid or an alkaline bisulphite. The reduced tellurium is then collected on a weighed filter, and carefully dried at gentle heat. If the solution is alkaline, it must be previously acidulated with hydrochloric acid; if it contains nitric acid, which might redissolve a portion of the precipitated tellurium, it must be boiled with hydrochloric acid till all the nitric acid is decomposed, then diluted with water, and treated with sulphurous acid as above. If the tellurium is in the state of telluric acid, that compound must first be reduced to tellurous acid by boiling with hydrochloric acid, and the tellurium then reduced by sulphurous acid.

Tellurium may be separated from the *alkalies* and *earths*, and from *manganese*, *iron*, *cobalt*, *nickel*, *zinc*, and *chromium*, by means of hydrosulphuric acid. If the precipitated sulphide of tellurium is quite pure and definite, it may be collected on a weighed filter, dried and weighed, and the amount of tellurium calculated from it. But if it contains excess of sulphur, which is often the case, it must be boiled with aqua-regia till it is completely decomposed; the solution filtered from the separated sulphur; freed from nitric acid in the manner above described; and the tellurium precipitated by sulphurous acid.

The separation of tellurium from *cadmium*, *copper*, and *lead*, may be effected by means of sulphide of ammonium, in which the sulphide of tellurium is easily soluble. The filtered solution is then treated with excess of hydrochloric acid to precipitate the sulphide of tellurium, which is then decomposed by aqua-regia as just described. Tellurium may be separated from *tin* in solution by means of sulphurous acid.

The quantity of metallic tellurium in an alloy may be estimated by heating the alloy in a current of chlorine gas; passing the volatile chloride of tellurium into water acidulated with hydrochloric acid, which dissolves it; and reducing the tellurium by sulphurous acid.

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ORDER VI.

METALS ISOMORPHOUS WITH PHOSPHORUS.

SECTION I.

ARSENIC.

Eq. 75 *or* 937·5.

This metal is found native, but more generally in combinanation with other metals, particularly cobalt and nickel, and is largely condensed, during the roasting of their ores, in the state of arsenious acid. The metal may be easily obtained, in a state of purity, by subliming a portion of native arsenic in a glass tube or retort, by the heat of a lamp, or by reducing a mixture of one part of arsenious acid and three parts of black flux, in the same apparatus. The metal in condensing forms a crust, of a steel-grey colour and bright metallic lustre. It has been observed to crystallise by sublimation in rhombohedral crystals, and is isomorphous with tellurium and antimony. It is a brittle metal, and very easily pulverised. The density of arsenic is from 5 to 5·96. It rises in vapour at 356° (180° Cent.) without first undergoing fusion. Arsenic vapour is colourless; its density is 10·370; and, like phosphorus and oxygen, its combining measure is one volume. It has as strong an effect upon the organ of smell as selenium; its odour resembles that of garlic. Arsenic combines in three proportions with oxygen, forming by spontaneous oxidation in air a grey sub-oxide, the composition of which is undetermined; it also forms arsenious and arsenic acids, AsO_3 and AsO_5.

Arsenious acid, 99 *or* 1237·5.—This compound is formed when metallic arsenic is volatilised in contact with the air. It is obtained in large quantity, as an accessary product, in the roasting of arsenical ores of tin, cobalt, and nickel, and as principal product in the roasting of arsenical pyrites. These operations are performed in reverberatory furnaces, communicating with chambers in which the arsenious acid condenses. The product is purified by a second sublimation in vessels of cast-iron, or, on a small scale, in glass or earthen retorts.

Arsenious acid heated in a tube closed at both ends melts into a colourless liquid; but under the ordinary atmospheric pressure, it volatilises at about 380° (at 444° according to Mitchell), without previous fusion, producing a colourless vapour, which has a density of 13·850, and is therefore composed of 1 volume of arsenic vapour and 3 volumes of oxygen, condensed into 1 volume. The vapour is inodorous when pure, but if the acid be volatilised in contact with any easily oxidisable substance, as when it is thrown on red-hot coals or iron, the garlic odour of metallic arsenic becomes perceptible.

In the solid state, arsenious acid exhibits three modifications, one amorphous, and two crystalline. (1.) When the sides of the vessel in which the acid is distilled become strongly heated, the vapour condenses, at a temperature near the melting point of the acid, into a transparent vitreous mass, having a conchoïdal fracture. (2.) When arsenious acid is sublimed in a glass tube, or under any circumstances which allow the vapour to condense suddenly, and solidify at once, without passing through the semi-fused state, it assumes the form of regular octohedrons, which, if the sublimation be slowly conducted, are distinct, and have an adamantine lustre. Similar octohedral crystals are obtained when arsenious acid separates from its solution in water or in ammonia. (3.) In the roasting of arsenical cobalt ores, arsenious acid is sometimes obtained in the form of thin transparent flexible plates, derived from a right rhombic prism (Wöhler). Crystals of similar form are obtained by saturating a boiling solution of caustic potash with arsenious acid, and then leaving it to cool or mixing it with water (Pasteur). Vitreous arsenious acid, even when completely protected from air and moisture, gradually loses its transparency, and becomes an opaque white mass, passing in fact into the octohedral variety.

The specific gravity of transparent vitreous arsenious acid is 3·7385, that of the octohedral variety 3·699 (Guibourt). The vitreous acid dissolves in water more quickly and more abundantly than the opaque crystalline acid; the same quantity of water which at 54° or 55° will take up 36 or 38 parts of the former, will not take up more than 12 or 14 of the latter (Bussy). According to Guibourt, on the contrary, 100 parts of boiling water dissolve 9·68 parts of the vitreous, and 11·47 of the opaque acid; and when the solutions are left to cool to 60°, the first retains 1·78 parts, and the latter 2·9 parts of the acid. The discrepancy of these statements and of various others respecting the solubility of arsenious acid, may perhaps be reconciled by the great facility with which the amorphous variety passes into the crystalline, and *vice versa.* It appears indeed that heat tends to transform the opaque into the vitreous acid, and cold to produce the contrary change, and this tendency is manifested even in presence of water. Thus the opaque acid is converted into the vitreous by long boiling with water, the contrary change taking place gradually in the solution when cold.

The aqueous solution of arsenious acid is transparent and colourless, and reddens litmus slightly. *Hydrosulphuric acid* colours it yellow, and on the addition of hydrochloric acid throws down a yellow precipitate of AsS_3. On the addition of a small quantity of ammonia, it gives a yellow precipitate with nitrate of *silver,* and a peculiar light green (Scheele's green) with sulphate of *copper;* these precipitates are easily soluble in excess of ammonia. Mixed with hydrochloric acid it produces a grey metallic deposit on *copper*. With *zinc* and sulphuric or hydrochloric acid, it evolves arseniuretted hydrogen gas (p. 211.).

Arsenious acid dissolves in many acids, in hydrochloric acid for example, with much greater facility than in water, but without forming any definite compounds. It is dissolved, however, by bitartrate of potash, with formation of a crystallisable salt analogous to the potash-tartrate of antimony. The vitreous acid dissolved in boiling dilute hydrochloric acid crystallises on cooling in regular octohedrons, the deposition of each crystal being accompanied by a flash of light. Agitation increases the number of crystals produced, and the intensity of the light. The opaque acid dissolved in hydrochloric acid does not emit any light on crystallising; the same is the case with the crystals obtained by cooling a solution of the vitreous acid in hydrochloric acid, when these crystals are redissolved in hydrochloric acid. Hence it appears that the vitreous acid dissolves *as such* in hydrochloric acid, and that the emission of light at the moment of crystallisation is due to the change from the amorphous to the crystalline state.

Arsenious acid is dissolved by *potash, soda,* and *ammonia,* also by *alkaline carbonates,* but from these latter solutions it is sometimes deposited in the free state, so that it is doubtful whether arsenious acid displaces carbonic acid in the humid way. The arsenites of the earths and metallic oxides are insoluble in water, but soluble in acids.

With potash, arsenious acid forms the salts $2KO \cdot AsO_3$, $KO \cdot AsO_3$, and $KO \cdot HO \cdot 2AsO_3$; similar salts with soda. With baryta, it forms $2BaO \cdot AsO_3$ and $BaO \cdot AsO_3$; and with lime, $2CaO \cdot AsO_3$. With nickel, cobalt, and silver, it forms bibasic and sesquibasic salts.

The neutral solutions of the alkaline arsenites give a yellow precipitate with nitrate of *silver*, and Scheele's green with *copper* salts. Acidulated with hydrochloric acid, they give with *hydrosulphuric acid,* &c., the same reactions as aqueous arsenious acid.

Nitric acid and *aqua regia* transform arsenious into arsenic acid. *Hydrogen, charcoal,* and other reducing agents easily reduce it to the metallic state.

Arsenious acid has a rough taste, slightly metallic, and afterwards sweetish. It is one of the most violent among acrid poisons.

The principal industrial use of arsenious acid is in calico-printing; it is also used in glass-making, serving to transform the protoxide of iron into sesquioxide, which produces glasses less highly coloured than the protoxide.

Arsenic acid, AsO_5, 115 *or* 1437·5.—This acid is obtained by heating powdered arsenious acid in a basin with an equal quantity of water, and adding nitric acid in small quantities to the mixture at the boiling point, so long as ruddy fumes escape. An addition of hydrochloric acid to the water is generally made, to increase the solubility of the arsenious acid, but it is not absolutely necessary. The solution of arsenic acid is then evaporated to dryness, to expel the remaining nitric and hydrochloric acids; but the dry mass must not be heated above the melting point of lead, otherwise oxygen gas is emitted and arsenious acid reproduced. Arsenic acid thus obtained is milk-white, and contains no water. Exposed to air, it slowly deliquesces, and runs into a liquid. But notwithstanding this, when strongly dried, it does not dissolve completely in water at once, and a portion of it appears to be insoluble; but the whole is dissolved by continued digestion. Arsenic acid, in absorbing moisture from the air, sometimes forms hydrated crystals, which are highly deliquescent; but this acid is easily made anhydrous, and does not retain basic water with force, like phosphoric acid. Its solution has a sour taste, and reddens vegetable blues. Arsenic acid, indeed, is a strong acid, and with the aid of heat expels all the volatile acids from their combinations. Arsenic acid undergoes fusion at a red heat, and at a higher temperature is completely dissipated in the form of arsenious acid and oxygen.

When an equivalent of arsenic acid is ignited with an excess of carbonate of soda, three equivalents of carbonic acid are expelled, and a *tribasic arseniate of soda* formed, which when dissolved in water, crystallises with 24 equivalents of water, forming the salt $3NaO . AsO_5 + 24HO$, isomorphous with the subphosphate of soda. The same salt is obtained by treating arsenic acid in solution with an excess of caustic soda. When carbonate of soda is added to a hot solution of arsenic acid, so long as there is effervescence, a salt is obtained by evaporation corresponding with the common phosphate of soda, containing 2 eq. of soda and 1 eq. of water as bases. This salt affects the same two multiples, in its water of crystallisation, as phosphate of soda, namely, 24HO and 14HO, but most frequently assumes the smaller proportion, forming the salt $2NaO . HO . AsO_5 + 14HO$. This arseniate is more soluble than the phosphate, and slightly deliquescent in damp air. When to the last salt a quantity of arsenic acid is added equal to that which it already contains, and the solution is highly concentrated, the salt named *biarseniate of soda* crystallises at a low temperature. This salt contains 1 eq. of soda and 2 eq. of water as bases, with 2 eq. of water of crystallisation, and corresponds with the biphosphate of soda. Its formula is $NaO.2HO.AsO_5 + 2HO$. The *biarseniate of potash*, which is analogous in composition, is a highly crystallisable salt. It is sometimes prepared by deflagrating arsenious acid with an equal weight of nitrate of potash. These arseniates of the alkalies, which contain water as base, all lose that element at a red heat; but, unlike the phosphates, they recover it when redissolved in water. Arsenic acid, therefore, forms only one, and that a tribasic class of salts. The arseniates of the earths and other metallic oxides are insoluble in water, but soluble in acids. *Arseniate of silver* ($3AgO . AsO_5$) falls as a precipitate of a chocolate-brown colour, when nitrate of silver is added to the solution of an arseniate, and affords an indication of the presence of arsenic acid. On treating a solution of arsenic acid with *ammonia* in excess, *chloride of ammonium*, and *sulphate of magnesia*, a white crystalline precipitate is formed, consisting of arseniate of magnesia and ammonia, $2MgO . NH_4O . AsO_5 + 12 Aq.$, similar in appearance and analogous in constitution to the ammonio-magnesian phosphate. *Hydrosulphuric acid* produces a yellow precipitate of AsS_5 after a considerable time; but if the solution be previously mixed with sulphurous acid, which reduces the arsenic acid to arsenious acid, a precipitate of AsS_3 is immediately produced.

Sulphides of arsenic.—When the bisulphide, realgar, is digested in caustic potash, it gives off sulphur and leaves a brownish black powder, having some resemblance to bioxide of lead, which, according to Berzelius, is the sulphide As_6S. *Bisulphide of arsenic*, AsS_2, is obtained by fusing sulphur with an excess of arsenic or arsenious acid. It is transparent and of a fine ruby colour after cooling, and may be distilled without decomposition. It forms the crystalline mineral realgar. *Sulpharsenious acid*, or *orpiment*, AsS_3, also occurs native. It may be prepared by decomposing a solution of arsenious acid in hydrochloric acid, by hydrosulphuric acid or by an alkaline sulphide. This sulphide has a rich yellow colour, and is the basis of the pigment called *king's yellow*. It is insoluble in acids, but soluble to a small extent in water containing hydrosulphuric acid, and also in pure water, but is precipitated by ebullition with a little hydrochloric acid. When heated, it fuses readily and becomes crystalline on cooling. It is readily dissolved by ammonia and solutions of the fixed alkalies, and is indeed a powerful sulphur-acid. *Sulpharsenic acid*, AsS_5, falls as a yellow precipitate, having much the appearance of orpiment, when a solution of arsenic acid somewhat concentrated is decomposed by hydrosulphuric acid. It may be sublimed without change, and after cooling forms a non-crystalline mass. It is also a powerful sulphur-acid, forming salts called *sulpharseniates*. *Persulphide of arsenic*, AsS_{18}, is obtained by precipitating neutral solution of sulpharseniate of potassium with alcohol, filtering the liquid, and evaporating off two-thirds of the alcohol; the concentrated solution, when left to cool, deposits the persulphide of arsenic in shining yellow crystalline laminæ.

Chlorides of arsenic.—A *terchloride*, $As\,Cl_3$, corresponding with arsenious acid, is formed when arsenic is introduced into chlorine gas, in which it takes fire and burns spontaneously. The same compound is obtained by distilling a mixture of 1 part of arsenic with 6 parts of corrosive sublimate; also by distilling arsenious acid with excess of hydrochloric acid, or of common salt and sulphuric acid. It is a colourless, oily, and very dense liquid, which is resolved by water into arsenious and hydrochloric acids. When a mixture of arsenic and calomel is distilled, a dark brown sublimate is formed, consisting partly of Hg_2ClAs, partly of Hg_4ClAs. No chloride corresponding with arsenic acid is known. *Bromide of arsenic*, $AsBr_3$, is formed by the direct combination of its elements. *Iodide of arsenic*, $As\,I_3$, is formed, according to Plisson, by digesting 3 parts of arsenic with 10 of iodine and 100 of water, as long as the odour of iodine is perceived. The liquid yields by evaporation red crystals of the iodide. *Fluoride of arsenic*, AsF_3, is obtained by distilling a mixture of fluor spar and arsenious acid with sulphuric acid. It is a fuming, colourless liquid; the density of its vapour is 2730 (Unverdorben).

Arsenic and hydrogen.—A solid arsenide of hydrogen was obtained by Davy, by using metallic arsenic as the negative pole (the chloroid) in decomposing water. Gay-Lussac and Thénard have also shown that the same compound precipitates when arsenide of potassium is dissolved in water. It is a chestnut-brown powder, which may be dried without change.

Its composition has not been determined with accuracy. *Arseniuretted hydrogen,* AsH_3, a gas analogous in constitution to ammonia, is obtained by dissolving arseniate of potassium or sodium in water, or an alloy of equal parts of zinc and arsenic in sulphuric acid diluted with three times its weight of water; or again, when zinc dissolves in hydrochloric or dilute sulphuric acid, with which arsenious acid is mixed:

$$6Zn + 3HO + AsO_3 + 6SO_3 = 6(ZnO \,.\, SO_3) + AsH_3.$$

It is a dangerous poison, when inhaled even in the most minute quantity, and should, therefore, be prepared with the greatest caution. The density of this gas is 2695 (Dumas). It is liquefied by a cold of —40°. When passed through a glass tube heated to redness by a spirit lamp, it is decomposed and deposits metallic arsenic. The flame of this gas, when burned in air, also deposits metallic arsenic upon a cold object exposed to it. No combination of arseniuretted hydrogen is known with either acids or bases. It precipitates many of the metallic solutions which are precipitated by hydrosulphuric acid, but not oxide of lead, its hydrogen alone being oxidated, and the arsenic being precipitated in combination with the metal. From the salts of silver, gold, platinum, and rhadium, it precipitates the metals, while arsenious acid remains in solution. This gas, when pure, is completely absorbed by a solution of sulphate of copper, and $AsCu_3$ precipitated.

TESTING FOR ARSENIC.

Poisoning from arsenious acid is much more frequent than from any other substance. Hence, a more than usual degree of importance is attached to the modes of detecting the presence of arsenic in minute quantity. Of the different preparations of the metal, arsenic acid, and after it arsenious acid, are the most poisonous; the salts and sulphides are so in a much less degree. Arsenious acid in the solid form and unmixed with foreign matters, is easily recognised as a white heavy powder, which is tasteless or nearly so, is entirely volatilised by heat, and diffuses a garlic odour in the reducing flame of a lamp. When dissolved in water, arsenious acid may be detected by the fluid tests, already mentioned (pp. 205, 206.). The silver and copper tests are most conveniently applied in the following forms.

1. *Ammonio-nitrate of silver.*—This is an exceedingly delicate test of arsenious acid, whether free, or in combination with an alkali. It is prepared by adding diluted ammonia to a solution of nitrate of silver, till the oxide of silver, which is first thrown down, is redissolved. When the ammonia has been added in proper quantity and not in excess, the odour of that substance is scarcely perceptible, and the liquid contains in solution the crystallisable ammonio-nitrate of silver, $AgO.NO_5 . 2NH_3$. This test-liquid throws down from arsenious acid, the yellow arsenite of silver, which is redissolved both by acids and by ammonia. A solution of nitrate of silver gives the same indication as the prepared ammonio-nitrate in an alkaline but not in an acid solution of arsenious acid. Nitrate of silver produces, in phosphate of soda or any other soluble phosphate, a yellow precipitate of phosphate of silver of the same colour as the arsenite of silver, and which might, therefore, be mistaken for the latter; but the action of the ammonio-nitrate is not liable to that ambiguity, as it does not produce a yellow precipitate in an alkaline solution of phosphoric acid, the phosphate of silver being then retained in solution by the ammonia of the reagent, although arsenite of silver is precipitated in the same circumstances. Both phosphate and arseniate of silver are indeed considerably more soluble in ammonia than the arsenite of the same metal.

2. *Ammonio-sulphate of copper* gives a beautiful green precipitate, the arsenite of copper, in both alkaline and acid solu-

tions of arsenious acid; sulphate of copper gives the same precipitate in the former, but not in the latter.

But in solutions containing organic matter, the indications of these tests are sometimes delusive, and often doubtful. Recourse is then had to the proper means of obtaining arsenic in the metallic form, from the liquid suspected to contain arsenious acid. Indeed, even where the indications of the fluid tests are clear, the reduction test should never be omitted, the evidence which it affords being of a superior and completely demonstrative character. The reduction test of arsenic is practised in two different ways: (1.) by the reduction of the sulphide of arsenic by means of charcoal and carbonate of potash, and (2.) by the production, and subsequent decomposition of the gaseous compound of arsenic and hydrogen. The following operations are necessary in the practice of the first method:—

REDUCTION TEST OF ARSENIC.

I. Preparation of the fluid:

1. Heat the mass with about one-fourth of its weight of strong sulphuric acid in a retort, to which is adapted a receiver having its inner surface wetted, till the organic matter is carbonised.
2. Pulverise the residue, and treat it with nitric acid mixed with a little hydrochloric acid, in order to bring the arsenic to the state of arsenic acid, which is easily soluble.
3. Boil with water; filter; and mix the filtrate with the liquid in the receiver.*

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* This is the mode of preparation most generally adopted, and it is applicable to all cases of searching for mineral poisons. Another method, which is especially applicable when the matter to be examined contains a large quantity of fat, is to heat the mass with strong hydrochloric acid, or aqua-regia, in

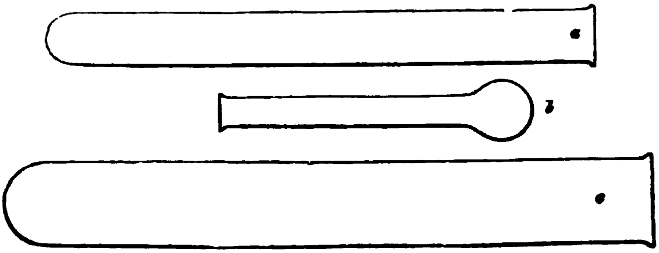
II. Precipitation of the sulphide of arsenic:

1. Transmit a stream of hydrosulphuric acid gas through the liquid for half an hour.*
2. Heat the liquid in an open vessel for a few minutes, to cause the precipitate to separate.
3. Wash the precipitate by affusion of water acidulated with hydrochloric acid, and subsidence.
4. Dry the precipitate at a temperature not exceeding 300°.

III. Reduction of the sulphide of arsenic:

1. Mix the dried precipitate intimately with twice its bulk of dry black flux (carbonate of potash and charcoal), or with a mixture of pounded charcoal and dry carbonate of soda, or with cyanide of potassium, and heat to redness in a glass tube, of the form and size of *a* or *b*, exhibited below.
2. Heat slowly a particle of the metallic crust in a glass tube *c*, and observe the formation of a white crystalline sublimate of arsenious acid.
3. Dissolve the sublimate in a small quantity of boiling water, and test with ammonio-nitrate of silver, &c., as above.

Fig. 8.



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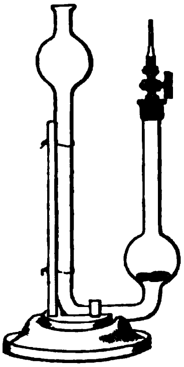
a large retort; the greater part of the arsenic is then converted into chloride, and may be collected in a receiver containing water.

* As the arsenic is in the state of arsenic acid, it is best to mix the liquid with sulphurous acid before passing the hydrosulphuric acid gas through it.

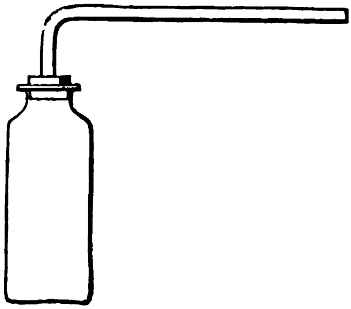
Marsh's test.—Hydrogen cannot be evolved in contact with any preparation of arsenic, soluble or insoluble, without combining with the metal, which is thus removed from the liquor, in the form of arseniuretted hydrogen gas. Mr. Marsh has founded, upon this fact, a simple and elegant mode of obtaining metallic arsenic from arsenical liquors. The stopcock being removed from the bulb-apparatus represented in the figure, a fragment of zinc is placed in the lower bulb, and diluted sulphuric acid poured upon it. The stopcock being replaced and closed, the lower bulb is soon filled with hydrogen gas, and the acid liquid forced into the upper bulb. It is necessary to test this hydrogen for arsenic, which will be found in it, if the zinc itself contains that metal. The gas for this purpose is kindled at the stopcock and allowed to burn with a small flame. If a stoneware plate be depressed upon the flame, a black spot of a steel-grey colour and bright metallic lustre, is formed, in a few seconds, upon the surface of the plate, supposing the gas to contain arsenic; or if a cold piece of glass be held over the flame, at a small height above it, a white sublimate of arsenious acid condenses upon the glass. But if the zinc employed contains no arsenic, neither of these effects is produced. The zinc being proved to be free from arsenic, a portion of the liquor to be tested is introduced into the lower bulb, in addition to the acid and zinc already there; and when the bulb is again filled with hydrogen gas, the latter is burned and examined precisely as before. If the liquor is loaded with organic matter, as generally happens with the liquids submitted to examination in actual cases of poisoning, the gas may be filled with froth, and the evolution of it very slow. But in the course of a night, the gas is

Fig. 9.



generally obtained in sufficient quantity, and in a proper state, to permit of examination. It is much better, however, first to remove the organic matter by one of the methods above given; the gas is then evolved freely and without frothing, and a plain bottle with a cork and glass jet will be sufficient for this reduction experiment. Then also, instead of burning the gas at the jet, it may be allowed to escape by a horizontal tube, such as that in figure 10., a portion of which is heated to redness by a spirit lamp. The arsenic condenses within the tube, beyond the flame and nearer the aperture, and forms a metallic crust, which may be converted by sublimation into arsenious acid; the sublimate may then be dissolved in a small quantity of boiling water, and the solution tested with ammonio-nitrate of silver, &c., as before.

Fig. 10.



When the liquid examined contains antimony, that metal combines with the nascent hydrogen, and comes off as antimoniuretted hydrogen, a gas which, when burned, or heated in a glass tube, gives the metal and a white sublimate, in the same circumstances as arsenic (L. Thompson). Antimony, however, may be recognised by a peculiarity of its reduction in the ignited tube. This metal is deposited in the tube, on both sides of the heated portion of it, and closer to the flame than arsenic, owing to the inferior volatility of antimony. The white sublimate also, if dissolved in water containing a drop of ammonia, will not give the proper indications with the fluid tests of arsenic, if the metal be antimony. Another distinction is, that the arsenical deposit is soluble in hypochlorite of soda, whereas the antimonial deposit is not.

Antidotes to arsenious acid.—When hydrated sesquioxide of iron is mixed with a solution of arsenious acid to the consistence of a thin paste, a reaction occurs by which the arsenious acid disappears in a few minutes, and the mass ceases to be poisonous. The arsenious acid takes oxygen from the sesquioxide of iron, and becomes arsenic acid, while the sesquioxide of iron is reduced to protoxide, a protarseniate of iron being the result, which is insoluble and inert:

$$2Fe_2O_3 + AsO_3 = 4FeO . AsO_5.$$

The constitution of this arseniate of iron is probably $2FeO.HO.AsO_5 + 2FeO$. Sesquioxide of iron, when used as an antidote to arsenious acid, should be in a gelatinous state, as it is obtained by precipitation, without drying. It may be prepared extemporaneously, by adding bicarbonate of soda in excess to any tincture or red solution of iron. Calcined magnesia may likewise be used as an antidote to arsenic. Care should be taken in preparing the latter not to employ too great a heat, which would render it very dense, and cause it to combine but slowly with the arsenious acid.

ESTIMATION OF ARSENIC, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

When arsenic is contained in a solution entirely in the form of arsenic acid, the best mode of estimating it is to precipitate it in the form of ammonio-magnesian arseniate, $2MgO . NH_4O . AsO_5 + 12HO$. The solution is mixed with excess of ammonia, and then with sulphate of magnesia, to which a quantity of chloride of ammonium has been added, sufficient to prevent the precipitation of the magnesia by ammonia. The liquid is then left to stand for about twelve hours; the precipitate collected on a weighed filter; washed with water containing ammonia; and dried over sulphuric acid in vacuo at ordinary temperatures; it has then the composition expressed by the above formula. It may also be dried, and more expeditiously, by exposing it to a temperature of exactly 212° F., whereby it loses 11 eq. of water, and is reduced to $2MgO.NH_4O.AsO_5 + HO$. Exposure to a higher temperature occasions loss of arsenic.

If the liquid contains arsenious acid, that compound may be converted into arsenic acid by mixing the solution with hydrochloric acid, and adding chlorate of potash by small quantities. The vessel must be left in a moderately warm place till the odour of free chlorine has entirely disappeared. Aqua regia may also be used to effect the oxidation, but it is less convenient. In either case, the liquid must be considerably diluted with water, otherwise part of the arsenic will be converted into chloride, and volatilised. It is best, perhaps, to perform the oxidation in a capacious retort having a receiver adapted to it.

Arsenious acid may also be estimated by its action on terchloride of gold. The arsenious acid is thereby converted into arsenic acid, and gold is precipitated in the metallic state. The quantity of gold thus reduced gives the quantity of arsenious acid present:

$$2AuCl_3 + 6HO + 3AsO_3 = 2Au + 6HCl + 3AsO_5.$$

The gold solution used for the purpose is the sodio-chloride, or ammonio-chloride of gold. It must be free from nitric acid; but the presence of hydrochloric acid, even in large excess, does not interfere with the action. The liquid, after the addition of the arsenic solution, must be left to itself for a considerable time to enable the gold to settle down completely.

When arsenic and arsenious acids exist together in solution the former may be precipitated as ammonio-magnesian arseniate (a considerable quantity of sal-ammoniac being added to prevent the simultaneous precipitation of the arsenious acid); the arsenious acid converted into arsenic acid by oxidation with chlorate of potash and hydrochloric acid, and then precipitated in a similar manner; or the arsenious acid may be estimated by chloride of gold, as last described.

The separation of arsenic in solution from the alkalies, earths, and those metals which are not precipitated from their acid solutions by hydrosulphuric acid, is effected by passing a stream of that gas through the acid liquid for a considerable time, then leaving it to stand, and heating it gently to ensure the complete precipitation of the sulphide of arsenic. If the arsenic is in the form of arsenic acid, that compound must be previously reduced to arsenious acid by means of sulphurous acid. The tersulphide of arsenic is collected on a weighed filter, thoroughly washed, and dried at a moderate heat. If quite pure, it may be weighed with the filter, and the quantity of arsenic thereby directly determined. But as it almost always contains an excess of sulphur, it is better to take a weighed quantity of it from the filter, oxidise it in a capacious flask by means of dilute hydrochloric acid and chlorate of potash, continuing the operation till the greater part of the sulphur is converted into sulphuric acid, and the remainder collects at the bottom of the liquid in a compact yellow globule; then decant the liquid, wash the globule of sulphur, and weigh it; and, finally, estimate the quantity of sulphur in the solution by precipitation with chloride of barium, adding the quantity thus found to the weight of the globule. The proportion of sulphur in the precipitated sulphide of arsenic being thus ascertained, the amount of arsenic is easily calculated.

From *cadmium*, *copper*, and *lead*, arsenic may be separated by means of sulphide of ammonium. The filtered ammoniacal solution is then treated with excess of hydrochloric or acetic acid to throw down the sulphide of arsenic, and the precipitate treated in the manner just described.

The separation of arsenic from *tin* is attended with considerable difficulty. One of the best methods is to convert the two metals into sulphides, and separate them, after drying and weighing the whole, by ignition in a stream of hydrosulphuric acid gas. The mixed sulphides are introduced into a weighed glass bulb, having a tube attached to it on each side. One of these tubes, the exit-tube, must be at least a quarter of an inch in diameter, to prevent stoppage, and bent downwards so as to dip into a flask containing ammonia. The whole is then weighed, hydrosulphuric acid gas passed through the apparatus, and the bulb heated till the whole of the sulphide of arsenic is sublimed. Part of the sulphide of arsenic passes into the ammoniacal liquid, by which it is dissolved, and the rest sublimes in the wide tube. When the operation is ended, and the apparatus has cooled, the wide tube is cut off at a short distance from the bulb, then broken, and the pieces digested in caustic potash to dissolve out the sulphide of arsenic. The solution thus obtained is added to the ammoniacal liquid in the flask; the sulphide of arsenic precipitated by hydrochloric acid, oxidised without previous filtration with hydrochloric acid and chlorate of potash; and the resulting arsenic acid precipitated by ammonia and sulphate of magnesia. The sulphide of tin remaining in the bulb is converted into stannic oxide by treating it with strong nitric acid.

When arsenic is combined with other metals in the form of an alloy, the whole may be dissolved or oxidised by means of aqua regia, or, better, with hydrochloric acid and chlorate of potash, and the arsenic separated by one of the preceding methods. In the case of tin, however, it is best to fuse the alloy in thin laminæ with five times its weight of carbonate of soda and an equal quantity of sulphur, whereby a mixture of sulpharseniate and sulphostannate of soda is obtained, which dissolves completely in hot water. The sulphides of tin and arsenic may then be precipitated by hydrochloric acid, and separated as above.*

SECTION II.

ANTIMONY.

Eq. 120·24 *or* 1503†; Sb (*stibium*).

This metal was well known to the alchemists, and is one of the metals the preparations of which were first introduced into medicine. Its sulphide is not an uncommon mineral, and is the source from which the metal and its compounds are always derived.

The sulphide of antimony is easily reduced to the metallic state by mixing together 4 parts of that substance, 3 parts of crude tartar, and 1½ parts of nitre, and projecting the mixture by small quantities at a time into a red hot crucible. The sulphide is also sometimes reduced by fusion with small iron nails, which combine with the sulphur and disengage the antimony. Or it may be obtained in a state of greater purity by strongly igniting in a crucible a quantity of the potash-tartrate of antimony, and placing the resulting metallic mass in water to remove any potassium it may have acquired.

Antimony is a white and brilliant metal, generally possessing a highly lamellated structure. It is easily obtained in rhombohedral crystals of the same form as arsenic and tellurium. Its density is from 6·702 to 6·86. It undergoes no change in the air. The point of fusion of antimony is estimated at 797°; it may be distilled at a white heat. This metal burns in air at a red heat, and produces copious fumes of oxide of antimony.

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* For a full account of the methods of estimating arsenic and separating it from other metals, *vide* H. Rose, "Handbuch der analytischen Chemie," 1851, ii. 381.

† The number 129, given by Berzelius for the equivalent of antimony, and hitherto generally adopted, appears from recent experiments by Schneider (Pogg. Ann. xcviii. 293) and by H. Rose (Berl. Akad. Ber. 1856, p. 229) to be much too high. Schneider, by reducing the tersulphide of antimony with hydrogen, finds the equivalent to be 120·24; and Rose, by decomposing the terchloride with hydrosulphuric acid, and precipitating the chlorine with nitrate of silver, finds the number 120·69.

Antimony combines in three proportions with oxygen, forming oxide of antimony and antimonic acid, SbO_3 and SbO_5, which correspond respectively with arsenious and arsenic acids; and antimonious acid, SbO_4, which is probably an intermediate or compound oxide, analogous to the black oxide of iron.

Teroxide of antimony, Antimonic oxide, Antimonious acid, SbO_3, 144·24 or 1803.—This oxide may be obtained by dissolving the sulphide, finely pounded and in the condition in which it is known as prepared sulphide of antimony, in four times its weight of concentrated hydrochloric acid. Pure hydrosulphuric acid goes off, and the antimony is converted into terchloride:

$$SbS_3 + 3HCl = SbCl_3 + 3HS.$$

The clear solution may be poured off, and precipitated at the boiling heat by a solution of carbonate of potash added in excess, the carbonic acid, which does not combine with oxide of antimony, escaping as gas. Teroxide of antimony, so prepared, is anhydrous, but is slightly soluble in water: it is white, but assumes a yellow tint when heated. It is fusible at a red heat, and sublimes at a high temperature in a close vessel, where it cannot pass into a higher state of oxidation. The brilliant crystalline needles which condense about antimony in a state of combustion likewise consist of this oxide. They possess the unusual prismatic form of arsenious acid observed by Wöhler. Oxide of antimony also crystallises as frequently in regular octohedrons, the other form of arsenious acid. It occurs in the prismatic form as a rare mineral, whose density is 5·227.

When a solution of potash is poured upon the bulky hydrate of teroxide of antimony, which is precipitated from the chloride by water, a portion of the oxide is dissolved, but the greater part loses its water, and is reduced in a few seconds to a fine greyish, crystalline powder, which is a neutral combination of teroxide of antimony with potash. Teroxide of antimony also combines with acids, forming the *salts of antimony*, or *antimonic salts*.

The solutions of these salts give with *hydrosulphuric acid* a brick-red precipitate of tersulphide of antimony, easily soluble in sulphide of ammonium, and reprecipitated by acids. This precipitate dissolves in strong boiling hydrochloric acid, forming the terchloride, which when thrown into water yields a precipitate of the oxychloride. This reaction with hydrosulphuric acid distinguishes antimony from all other metals.* *Zinc* or *iron* precipitates antimony from its solutions in the form of a black powder, which, when fused on charcoal before the blow-pipe, yields a brittle button of the metal. According to Dr. Odling†, antimony is also precipitated by *copper*, in the form of a brilliant metallic film, which may be dissolved off the copper by a solution of permanganate of potash, yielding a solution which will give the characteristic red precipitate with hydrosulphuric acid. This reaction affords a ready method of separating antimony from liquids containing organic matter,—as in medico-legal inquiries. All compounds of antimony fused upon charcoal with *carbonate of soda* or *cyanide of potassium*, yield a brittle globule of antimony, a thick white fume being at the same time given off, and the charcoal covered to some distance around with a white deposit of antimonic oxide. The reduction with cyanide of potassium may also be performed in a porcelain crucible, without charcoal. A solution of *terchloride of gold* added to the solution of a salt of teroxide of antimony, forms a yellow precipitate of metallic gold, the oxide of antimony being at the same time converted into antimonic acid, which compound is precipitated as a white powder, together with the gold, unless the solution contains a very large excess of hydrochloric acid. In a solution of oxide of antimony in potash, terchloride of gold produces a black precipitate, which is not altered by heating. This reaction is extremely delicate.

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* For the reactions of antimonic salts with alkalies, see *terchloride of antimony* and *tartar-emetic*.

† Guy's Hospital Reports, [3.] ii. 249.

Tersulphide of antimony, SbS_3, 168·24 or 2103.—The common ore of antimony is a tersulphide, SbS_3, corresponding with the preceding oxide of antimony. It is rarely free from sulphide of arsenic, which thus often enters into the antimonial preparations derived from the sulphide of antimony, but into tartar-emetic less frequently than the others. The same sulphide is formed when salts of the oxide of antimony, such as tartar-emetic, are precipitated by hydrosulphuric acid; but it is then of an orange-red colour. When the precipitated sulphide is dried, it loses water and becomes anhydrous, still remaining of a dull orange colour; but when heated more strongly, it shrinks at a particular temperature, and assumes the black colour and metallic lustre of the native sulphide. This sulphide is also obtained of a dark brown colour by boiling the prepared sulphide of antimony in a solution of carbonate of potash, and allowing the solution to cool; by fusing 2½ parts of the prepared sulphide with 1 part of carbonate of potash; or dissolving it in a boiling solution of caustic potash, and afterwards adding an acid. The last preparation is known as *Kermes mineral.* It has a much duller colour than the precipitated sulphide, but differs from it only in containing small quantities of oxide and pentasulphide of antimony, together with an alkaline sulphide which cannot be removed by washing (Berzelius). When the cooled mother-liquor from which kermes is deposited is mixed with hydrochloric acid, a precipitate is obtained, consisting, like the kermes, of SbS_3 mixed with SbO_3 and SbS_5, but of a redder colour. It is sometimes called the *golden sulphuret of antimony*.

When the sulphide of antimony is oxidated at a red heat, much sulphur is burned off, and an impure oxide of antimony remains. This matter forms, when fused, the *glass of antimony*, which contains a considerable quantity of undecomposed sulphide. The glass, reduced to powder, is boiled with bitartrate of potash as a source of oxide of antimony, in the pharmaceutical preparation of tartar-emetic. The oxide of antimony is dissolved out from the glass by acids, and a substance is left which is called *saffron of antimony*. This last is a definite compound of oxide and sulphide of antimony, $SbO_3 . 2SbS_3$, which also occurs as a mineral—namely, red antimony ore.

Terchloride of antimony, $SbCl_3$, is obtained by distilling either metallic antimony or the tersulphide of antimony with corrosive sublimate. When heated it flows like an oil, and becomes a crystalline mass on cooling. It is a powerful cautery. This salt deliquesces in air, and becomes turbid, owing to the deposition of a subsalt. A concentrated solution of chloride of antimony is also obtained by dissolving the sulphide of antimony in hydrochloric acid. When this solution is thrown into water, it gives a white bulky precipitate, which after a time resolves itself into groups of small crystals, having usually a fawn colour; it was formerly called the *powder of Algaroth*. These small crystals are an oxychloride of antimony, which, according to the analyses of Johnston and Malaguti, contains $2SbCl_3 . 9SbO_3$.

A solution of terchloride of antimony, to which water is added, and then a sufficient quantity of hydrochloric acid to redissolve the precipitate thereby produced, gives with *potash* a white precipitate of the hydrated teroxide, soluble in a very large excess of the alkali. *Ammonia* forms the same precipitate insoluble in excess. *Carbonate of potash*, or *soda*, produces also a white precipitate of the hydrated teroxide, which is soluble in excess, especially of the potash-salt, but reappears after a while. These reactions are greatly modified by the presence of fixed organic acids, especially of tartaric acid. In such a case, water forms no precipitate, ammonia but a slight one and after some time only, and the precipitate formed by potash dissolves easily in excess of the alkali. (See *Tartar-emetic.*)

Terfluoride of antimony, SbF_3, is obtained, by treating the teroxide with strong hydrofluoric acid, in colourless crystals which dissolve in water without decomposition. It unites with fluoride of potassium, forming the compound $3KF . SbF_3$ and similarly with fluoride of sodium and fluoride of ammonium.

Sulphate of antimony, $SbO_3 . 3SO_3$, is obtained, by boiling metallic antimony with concentrated sulphuric acid, as a white saline mass, which is decomposed by water.

Oxalate of potash and antimony, $KO . C_2O_3 + SbO_3 . 3C_2O_3$. —This is a double crystallisable salt of antimony, which, like the tartrate of potash and antimony, may be dissolved in water without decomposition. It is prepared by saturating binoxalate of potash with oxide of antimony. It is soluble at 48° in ten times its weight of water (Lassaigne). According to Bussy, when binoxalate of potash is digested upon oxide of antimony in excess, two salts are formed, one in oblique prisms, and another less soluble, in intricate small crystals; but neither is very stable. The former is decomposed by a large quantity of water: its analysis gave $3(KO . C_2O_3) + SbO_3 . 3C_2O_3 + 6HO$.*

Tartrate of potash and antimony, $KO . SbO_3 + C_8H_4O_{10} . 2HO$. —This salt, the tartar-emetic or potash tartrate of antimony of pharmacy, is prepared by neutralising bitartrate of potash with oxide of antimony; the oxide obtained by decomposing the chloride or sulphate of antimony with water answers best for the purpose. A quantity of oxide of antimony may be boiled with three or four times its weight of water, and bitartrate of potash added in small quantities till the oxide is entirely dissolved. The filtered solution yields the salt, on cooling, in large transparent crystals, the form of which is an octohedron with a rhombic base; they become white in the air, and lose their water of crystallisation. They are soluble in 14 times their weight of cold water, and in 1·88 parts of boiling water, but not in alcohol. The mother-liquor of these crystals becomes a syrupy liquid, and dries up into a gummy mass without crystallising, when oxide of antimony has been dissolved in excess by the acid tartrate in preparing the salt. *Potash* added to a solution of the salt throws down the teroxide of antimony, but the precipitate is easily soluble in excess of potash. *Ammonia* forms no precipitate at first, and but a slight one after standing. *Alkaline carbonates* form a precipitate of the teroxide insoluble in excess of the reagent. With *hydrosulphuric acid*, the reaction is the same as with other salts of antimony. (See p. 224.) Salts of the earths and basic metallic oxides, such as *baryta* and *oxide of silver*, throw down from its solution a compound of the tartrate of antimony with tartrate of baryta, tartrate of silver, &c. (Wallquist.) Strong acids decompose the salt, and produce a precipitate which is a mixture of bitartrate of potash with oxide of antimony, or with a subsalt of that oxide.

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* J. Pharm. 1838, p. 509.

This salt was formerly described as a double tartrate of potash and antimony, or, abstracting its water of crystallisation, which is differently stated at 2 and 3 equivalents, as $KO.(C_4H_2O_5)+SbO_3.(C_4H_2O_5)$. When the atomic weight of tartaric acid is doubled, and it is represented as a bibasic acid, the formula for dry tartar-emetic becomes $KO.SbO_3.(C_8H_4O_{10})$. In comparing the last formula with that of bitartrate of potash, represented also as a bibasic salt, $KO.HO.(C_8H_4O_{10})$, it is observed that 1 eq. of oxide of antimony takes the place of 1 eq. of water as base, although the former contains 3 eq. of oxygen, and the latter only one. Tartrate of potash and antimony is, in this respect, an anomalous salt. Another equally remarkable fact respecting this salt has been observed by M. Dumas, namely, that 2 eq. of water are separated from the anhydrous salt at 428°, leaving a substance of which the elements are $C_8H_2O_{12}$ SbK. The first part of this formula $C_8H_2O_{12}$, M. Dumas looks upon as a quadribasic salt-radical, existing in the tartrates, which in hydrated tartaric acid is united with 4H, in bitartrate of potash with 3H + K, and in tartrate of antimony and potash with Sb + K. Here Sb is found equivalent to and capable of replacing 3H. Tartrate of antimony and potash might, therefore, be represented by $KSb(C_8H_2O_{12}) + 2HO +$ water of crystallisation. If SbO_2 be regarded as a radical capable of replacing 1 eq. of hydrogen (similar to uranyl, U_2O_2, the hypothetical radical of the uranic salts), the formula of tartar-emetic dried at 212° may be written as $C_8H_4K(SbO_2)O_{12}$, and that of the salt dried between 392° and 428°, as $C_8H_2K(SbO_2)O_{10}$.

Antimonic acid, SbO_5,160·24 *or* 2003.—This compound is obtained in the hydrated state: 1. By treating antimony with nitric acid, or with aqua-regia containing excess of nitric acid. 2. By decomposing pentachloride of antimony with water. 3. By precipitating a solution of antimoniate of potash with an acid.

The hydrated acid obtained by either of these methods gives off its water at a moderate heat, and yields *anhydrous antimonic acid* in the form of a yellowish powder, which is tasteless, insoluble in water, decomposes alkaline carbonates, and, when heated to redness, gives off oxygen, and is converted into antimoniate of antimonic oxide, $SbO_3 . SbO_5$.

The hydrates obtained by the three methods above described are by no means identical. The acid in the first is monobasic, whereas in the other two it is bibasic. The bibasic acid is distinguished by the name of *metantimonic acid,* while the monobasic acid is called simply *antimonic acid* (Fremy).

Antimonic acid forms neutral or normal salts, containing $MO.SbO_5$, and acid salts whose formula is $MO.(SbO_5)_2$. Metantimonic acid forms neutral salts containing $(MO)_2.SbO_5$, and acid salts containing $(MO)_2.(SbO_5)_2$, or $MO.SbO_5$, so that the acid metantimoniates are isomeric or polymeric with the neutral antimoniates. An acid metantimoniate easily changes into a neutral antimoniate. The metantimoniates of potash, soda, and ammonia are crystalline; the antimoniates of the same bases are gelatinous and uncrystallisable. The soluble acid metantimoniates form a crystalline precipitate with salts of soda; the soluble antimoniates do not form any such precipitate (Fremy).

Antimoniates of potash.—The neutral salt, $KO.SbO_5.5HO$, is obtained by fusing 1 part of antimony with 4 parts of nitre, digesting the fused mass in tepid water to remove nitrate and nitrite of potash, and boiling the residue for an hour or two with water. The white insoluble mass of anhydrous antimoniate is thereby transformed into a hydrate containing 5 eq. water, which is soluble. The solution when evaporated leaves this hydrate in the form of a gummy uncrystallisable mass, which gives off 2 eq. of water at 320°, and the whole at a higher temperature.

Acid antimoniate of potash, $KO.(SbO_5)_2$ is obtained by passing carbonic acid gas through a solution of the neutral antimoniate. It is white, crystalline, perfectly insoluble in water, and is converted into the neutral salt when heated with excess of potash. This salt is the *antimonium diaphoreticum lavatum* of the pharmacopœias (Fremy).

Neutral metantimoniate of potash, $2KO.SbO_5$, is prepared by fusing antimonic acid or neutral antimoniate of potash with a large excess of potash. The fused mass dissolves in a small quantity of water, and the solution evaporated in vacuo yields crystals of the neutral metantimoniate. This salt dissolves freely and without decomposition in warm water containing excess of potash; but cold water or alcohol decomposes it into potash and the acid metantimoniate. Hence the aqueous solution of this salt gives a precipitate, after a while, with salts of soda (Fremy).

Acid metantimoniate of potash, $KO . SbO_5 + 7HO$, sometimes called *granular antimoniate of potash.*—This salt is used as a test for soda. To obtain it, the neutral antimoniate is first prepared and dissolved in the manner above described; the solution filtered to separate any acid antimoniate that may remain undissolved; then evaporated to a syrup in a silver vessel; and hydrate of potash added in lumps to convert the antimoniate into metantimoniate. The evaporation is continued till the liquid begins to crystallise, which is ascertained by taking out a drop now and then upon a glass rod, and the liquid is left to cool. A crystalline mass is thus obtained, consisting of neutral and acid metantimoniate of potash; the alkaline liquor is then decanted, and the salt dried upon filtering paper or unglazed porcelain (Fremy). This salt may also be prepared by treating terchloride of antimony with an excess of potash sufficient to redissolve the precipitate first formed, and adding permanganate of potash till the solution acquires a faint rose colour. The liquid, filtered and evaporated, yields crystals of the granular metantimoniate (Reynoso). This salt is sparingly soluble in cold water, but dissolves readily in water between 113° and 122°. When boiled with water for a few minutes, or kept in contact with water for some time, it is converted into the neutral antimoniate. It must therefore be preserved in the solid state, and dissolved just before it is required for use. A small quantity of it is then treated with about twice its weight of cold water to remove excess of potash, and convert any neutral metantimoniate into the acid salt; the liquid decanted; the remaining salt rapidly washed three or four times with cold water; then left in contact with water for a few minutes, and the liquid filtered. On adding to the solution thus obtained, a small quantity of any soda-salt, a crystalline precipitate is formed, consisting of *acid metantimoniate of soda,* $NaO . SbO_5 + 7HO$. This reaction is apparent in a solution containing only 1 part of soda in 300. In strong solutions of soda, the precipitate appears immediately, but in dilute solutions only after a while, the crystals being deposited on the sides of the vessel. An excess of potash in the reagent also retards the precipitation (Fremy*).

Antimoniates of ammonia.—When the metantimonic acid, obtained by decomposing pentachloride of antimony with water, is treated with ammonia, part of it dissolves, and a solution is formed containing *neutral metantimoniate of ammonia.* A few drops of alcohol added to the solution, throw down a precipitate consisting of *acid metantimoniate of ammonia,* $NH_4O . SbO_5 + 6HO$. This salt is slightly soluble, and its solution precipitates soda-salts. It changes spontaneously in a few days, even when kept in a close vessel, into neutral *antimoniate* of ammonia, which is completely insoluble in water. The same change is instantly produced in it by heat (Fremy).

Antimoniate of lead, $PbO . SbO_5$, may be obtained as a yellow powder by fusing antimonic acid with oxide of lead, or as a white hydrate by precipitation: the hydrate gives off its water when heated, and turns yellow. This salt is used as a pigment under the denomination of *Naples yellow.*

Antimoniate of antimony, $SbO_3 . SbO_5$. or SbO_4, is obtained by the action of heat upon antimonic acid, by roasting the teroxide or tersulphide, or by treating powdered antimony with excess of nitric acid. It is white, infusible, and unalterable by heat; slightly soluble in water. It was formerly regarded as a distinct acid, SbO_4, and called *antimonious acid;* but it does not form salts; and, when boiled with bitartrate of potash, it is resolved into cream of tartar, which dissolves, and a residue of antimonic acid.

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* Traité de Chimie Générale, par Pelouze et Fremy, 2me. ed. t. 3. pp. 151. 157. According to Heffter (Pogg. Ann. lxxxvi. 418.), the granular antimoniate of potash is $KO . HO + 12(KO . SbO_5 + 7HO)$; the precipitated soda-salt is similarly constituted; and by treating the solution of this salt in boiling water with salts of the earths and metallic oxides, precipitates are obtained, also of similar composition, or differing only in the water which they contain. Heffter's formulæ were calculated according to the old equivalent of antimony, 129; but Schneider has shown that, on re-calculating the analyses with the lower equivalent 120·24, the numbers of the equivalents of base and acid come out equal.

Pentasulphide of antimony, Sulphantimonic acid, SbO_5, is obtained by passing hydrosulphuric acid gas into an acid solution of pentachloride of antimony, or into the solution of an alkaline antimoniate. It has an orange-colour much less red than the tersulphide; it is the *golden sulphuret of antimony* of several pharmacopœias. It combines with basic metallic sulphides, forming the *sulphantimoniates.* The *sodium-salt,* $3NaS . SbS_5$, which is sometimes used in medicine, is obtained by mixing 18 parts of finely pounded tersulphide of antimony, 12 parts of dry carbonate of soda, 13 parts of lime, and 3½ parts of sulphur; triturating the mixture for about half an hour; leaving it for two or three days in a flask filled with water, and shaking it from time to time; then filtering and evaporating, first over the open fire, afterwards in vacuo. The salt is thus obtained in large regular tetrahedrons of a pale yellow colour. It is very soluble in water, and is decomposed by acids, which throw down hydrated pentasulphide of antimony.

Pentachloride of antimony, $SbCl_5$, is obtained by heating metallic antimony in a current of dry chlorine, and distilling the product in a dry retort, rejecting the first portions of the distillate, which contain excess of chlorine. It is a yellowish, very volatile liquid, which emits suffocating vapours. Water first converts it into a crystalline hydrate, and then decomposes it, forming antimonic acid: $SbCl_5 + 5HO = SbO_5 + 5HCl$. It absorbs ammonia and phosphuretted hydrogen, forming red-brown solid compounds. It absorbs olefiant gas as readily as chlorine, and forms Dutch liquid. It likewise absorbs hydrosulphuric acid gas at ordinary temperatures, forming a white crystalline mass, consisting of *chlorosulphide of antimony*, $SbCl_3S_2$, exactly analogous to chlorosulphide of phosphorus PCl_3S_2. Pentasulphide of antimony, treated with dry chlorine aided by heat, forms a white pulverulent compound, containing $SbCl_8S_3$, or $SbCl_5.3SCl$; this compound is decomposed at 572° (300° C.) into chlorine, chloride of sulphur, and terchloride of antimony. Pentachloride of antimony combines with hydrocyanic acid, forming a white, crystalline, volatile compound, composed of $SbCl_5.3HCy$. It also combines with chloride of cyanogen.

Antimoniuretted hydrogen.—This compound is obtained by dissolving an alloy of zinc and antimony in hydrochloric or dilute sulphuric acid, or by dissolving zinc in either of these dilute acids containing oxide or chloride of antimony, tartar-emetic, &c. The gas, however, always contains more or less free hydrogen. Its comparative purity may be tested by means of a solution of nitrate of silver, which absorbs the antimoniuretted hydrogen, and leaves the free hydrogen. An alloy of 2 parts zinc and 1 part antimony yields the purest gas; an alloy containing a larger proportion of antimony gives more free hydrogen; and an alloy of equal parts of the two metals yields scarcely anything but free hydrogen. As the compound has never been obtained in a state of purity, its composition has not been correctly ascertained, but it is probably SbH_3.

Antimoniuretted hydrogen is a colourless gas, and when free from arsenic, quite inodorous. It is insoluble in water, and in alkaline liquids; with solutions of silver or mercury it forms precipitates containing silver or mercury, together with antimony. When burned from a jet, it deposits, on a plate of porcelain, metallic spots, greatly resembling those of arsenic, but differing from the latter in possessing less lustre and in not being soluble in hypochlorite of soda. They may also be dissolved in aqua-regia or in permanganate of potash (p. 224), and the solution will give the characteristic orange precipitate with hydrosulphuric acid. A metallic deposit may also be obtained by heating a glass tube through which the gas is passed; and this deposit, when sublimed, will not exhibit the characters of arsenic (p. 216).

Alloys of antimony with *potassium* or *sodium* may be obtained by igniting metallic antimony, or its oxide or sulphide, with an organic salt of potash or soda. Thus, when 5 parts of crude tartar and 4 parts of antimony are slowly heated in a covered crucible till the mixture becomes charred, then heated to whiteness for an hour, and left to cool, a crystalline regulus is obtained containing 12 per cent. of potassium. This alloy decomposes water rapidly, and oxidises slowly in the air when in the compact state, but becomes heated and takes fire when rubbed to powder.

A mixture of 7 parts of antimony and 3 parts of *iron*, heated to whiteness in a crucible lined with charcoal, forms a white, very hard, slightly magnetic alloy, which gives sparks when filed. It is always formed when sulphide of antimony is reduced by iron in excess.

With *zinc*, antimony forms alloys of definite crystalline character. A fused mixture of the two metals, containing from 43 to 70 per cent. of zinc, deposits by partial cooling, silver-white rhombic prisms, containing from 43 to 64 per cent. of zinc. The alloy containing exactly 43 per cent. of zinc, appears to be a definite compound, *stibiotrizincyl*, $SbZn_3$. Mixtures containing from 33 to 20 per cent. of zinc deposit rhombic crystals containing from 35 to 21 per cent. of zinc. The alloy containing exactly 33 per cent. is *stibiobizincyl*, $SbZn_2$. These alloys, especially $SbZn_3$, decompose water with evolution of hydrogen at the boiling heat, and very rapidly under the influence of acids (J. P. Cooke *).

Type-metal, is an alloy of antimony and lead, usually containing 76 per cent. of lead, which corresponds nearly with the formula Pb_2Sb.

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* Sill. Am. J. [2.] xviii. 229; xx. 222.

ESTIMATION OF ANTIMONY, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Antimony cannot be estimated in the form of antimonious or antimonic acid, because we can never be sure of the purity of those bodies. The best mode of proceeding is to precipitate it by hydrosulphuric acid, collect the sulphide of antimony on a weighed filter, and, after ascertaining the total quantity of the precipitate, estimate the proportion of sulphur in it in the manner already described with reference to sulphide of arsenic (p. 219). Or the sulphide of antimony may be decomposed by heating it in a current of hydrogen gas, whereupon hydrosulphuric acid and sulphur-vapour escape, and metallic antimony remains behind. For this purpose, a weighed portion of the sulphide is placed in a small porcelain crucible having a hole in its cover, through which a tube passes to convey the hydrogen. The temperature is gradually raised, and the process continued till the weight of the crucible no longer varies. The reduction may also be performed in a bulb-tube.

When antimonious and antimonic acids occur together in solution, the total quantity of antimony may be ascertained by treating one portion of the liquid in the manner just described, and the quantity existing as antimonious acid may be determined in another portion by means of terchloride of gold, 2 eq. of precipitated gold corresponding to 3 eq. of antimonious acid:

$$2AuCl_3 + 6HO + 3SbO_3 = 2Au + 6HCl + 3SbO_5.$$

The separation of antimony from the *alkalies* and *earths*, and from those metals which are not precipitated from their acid solutions by hydrosulphuric acid, is effected by means of that reagent.

To separate antimony from *cadmium*, *copper*, and *lead*, the solution, after being neutralised with ammonia, is mixed with sulphide of ammonium containing excess of sulphur. The sulphide of antimony then dissolves, the other sulphides remaining undissolved; and on mixing the filtrate with acetic acid (hydrochloric acid might redissolve a portion of the precipitate, especially as the liquid becomes heated), the sulphide of antimony is reprecipitated, and may be treated as above.

When antimony is combined with any of the preceding metals in the form of an alloy, it may be separated by treating the alloy with nitric acid, whereby the other metals are dissolved, and the antimony converted into insoluble antimonic acid. This method is, however, not rigidly exact; for the nitric acid dissolves a small portion of the antimony.

Separation of antimony from arsenic and tin.—The separation of these metals is attended with considerable difficulty. The best mode of effecting it is to convert them into arseniate, stannate, and antimoniate of soda, and treat the mixture with dilute alcohol, which dissolves the arseniate and stannate of soda, and leaves the antimoniate undissolved.

If the three metals exist together in solution, they must be precipitated as sulphides by hydrosulphuric acid, and the precipitate treated by one of the following methods: —

(1.) The precipitated sulphides are fused in a silver crucible with a mixture of hydrate of soda and nitre: or, better, they are oxidised by heating them with strong nitric acid; the solution, together with the insoluble stannic and antimonic acids, mixed with excess of caustic soda, and evaporated to a small bulk; then transferred to a silver crucible, evaporated to dryness, and kept for some time in a state of red hot fusion. The fused mass, consisting of arseniate, stannate, and antimoniate of soda, is disintegrated by digestion in warm water; the contents of the crucible transferred to a beaker-glass; and the crucible well rinsed out with a *measured* quantity of water. The greater part of the arseniate and stannate of soda then dissolves, while the antimoniate remains undissolved. But to effect complete separation, a quantity of alcohol of sp. gr. 0·838 is added, equal in bulk to one-third of the water used; the mixture left to stand for 24 hours and frequently stirred; and the antimoniate of soda, which has then completely settled down, is collected on a filter and washed, first, with a mixture of 1 volume of the same alcohol to 3 vols. of water, then with 1 vol. alcohol to 2 vols. water; next, with a mixture of equal measures of water and alcohol; and, lastly, with 3 vols. alcohol to 1 vol. water (H. Rose).*

(2.) The precipitated sulphides of the three metals are dissolved in a mixture of sulphide of sodium and caustic soda, and the liquid mixed with a solution of hypochlorite of soda. The sulphides are thereby oxidised and converted into arsenic, stannic, and antimonic acids, which combine with the soda, and may be separated by treatment with dilute alcohol, and washing, as in Rose's process. This method is due to Dr. Williamson; it is easier of execution than the former, as the fused mixture of the soda-salts is very hard, and difficult to disintegrate by water.

The antimoniate of soda, separated by either of these processes, is digested in a mixture of hydrochloric and tartaric acids, which dissolves it completely; the antimony then precipitated by hydrosulphuric acid; and its quantity estimated in the manner already described (p. 235).

The filtrate containing the arseniate and stannate of soda is supersaturated with hydrochloric acid, which throws down a bulky precipitate of arseniate of stannic oxide; hydrosulphuric acid gas passed through the liquid till the white precipitate is completely converted into a brown mixture of the sulphides of tin and arsenic; the whole left to stand till the odour of hydrosulphuric acid is no longer perceptible; the precipitate collected on a weighed filter; and the filtrate heated for some time to expel the greater part of the alcohol; then mixed with sulphurous acid, and again treated with hydrosulphuric acid, whereby a small quantity of sulphide of arsenic is generally precipitated. This quantity of sulphide of arsenic being quite free from tin, need not be added to the mixed sulphides on the filter.

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* Handb. d. anal. Chem. 1851. ii. 429.

These mixed sulphides are dried at 212°, their total weight determined, and a known quantity heated in a stream of hydrosulphuric acid gas in the manner described at page 220. The residual sulphide of tin is then converted into stannic oxide, and the sublimed sulphide of arsenic, together with the small quantity separately precipitated, is converted into arsenic acid by treatment with hydrochloric acid and chlorate of potash, and the arsenic precipitated as ammonio-magnesian arseniate (H. Rose).

If the three metals are in the state of solid oxides, the mixture may be dissolved in hydrochloric acid, with addition of tartaric acid, and the metals precipitated as sulphides as before. If the metals are mixed in the form of an alloy, they may be dissolved in aqua-regia, the solution mixed with tartaric acid, then diluted, and precipitated in the same manner.

The method just described may, of course, be applied to the separation of antimony from tin or from arsenic alone. In these cases, however, simpler methods may often be advantageously adopted.

Separation of antimony from tin—When these two metals exist together in solution, and the sum of their weights is known, the separation may be effected, and the weights of the two determined, by immersing in the solution a piece of pure tin, which precipitates the antimony in the form of a black powder. To render the precipitation complete, a gentle heat must be applied, and the solution must contain excess of acid. The antimony is collected on a weighed filter, dried at a gentle heat, and weighed. If the sum of the weights is not previously known, the metals must be precipitated together by zinc from a known quantity of the solution, and the antimony precipitated by tin from another portion. When the two metals exist together in an alloy, a portion of the alloy must be weighed, then dissolved in aqua-regia, and the solution mixed with tartaric acid, diluted with water, and treated as above.

Another method of separation is to precipitate the two metals with zinc, and treat the precipitate with strong hydrochloric acid without previously decanting the solution of chloride of zinc. The tin then dissolves, while the antimony remains undissolved, the presence of the chloride of zinc diminishing its tendency to dissolve in the acid. The tin may afterwards be precipitated by hydrosulphuric acid, and the sulphide converted into stannic oxide, by treating it with strong nitric acid (Levol).*

Separation of antimony from arsenic.—When these two metals are associated in the metallic state, they may be completely separated by heating the alloy in a stream of carbonic acid, the arsenic then volatilising, and the antimony remaining. Antimony is, however, the only metal from which arsenic can be completely separated in this manner; hence, if the alloy contains any other metal, some of the arsenic will be retained, and the method is no longer applicable.

When this is the case, the alloy may be dissolved in aqua regia, or in hydrochloric acid to which chlorate of potash is gradually added; the solution diluted with water after addition of tartaric acid; then mixed with a considerable quantity of chloride of ammonium and excess of ammonia; and the arsenic precipitated as ammonio-magnesian arseniate by addition of sulphate of magnesia. The antimony may then be precipitated from the filtrate by hydrosulphuric acid.

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* Ann. Ch. Phys. [3.] xiii. 125.

SECTION III.

BISMUTH.

Eq. 213, *or* 2662·5; Bi.

Bismuth is generally found in the metallic state, disseminated in quartz-rock; but occurs also as an oxide, carbonate, and sulphide, either alone or associated with other metals; also in combination with tellurium. Native bismuth is, however, the only mineral which occurs in sufficient abundance for the economical extraction of the metal. The process of extraction as performed in Saxony, whence all the bismuth of commerce is obtained, is very simple, the mineral being merely heated in close vessels, so as to melt the bismuth, and thereby separate it from the gangue or accompanying rock. The fusion is performed in iron tubes, laid in an inclined position, in a furnace. (*Fig.* 11.) The ore is introduced at the upper end, *d*, which is then plugged. The other end, *b*, is closed with an iron plate having an aperture, *o*, through which the melted metal runs into earthen pots, *a*, heated by a few coals placed in the space, *K*, below, so as to keep the metal in the melted state. It is then ladled out and run into moulds. The crude metal thus obtained is afterwards fused with 1-10th of its weight of nitre, to free it from sulphur, arsenic, and certain foreign metals.

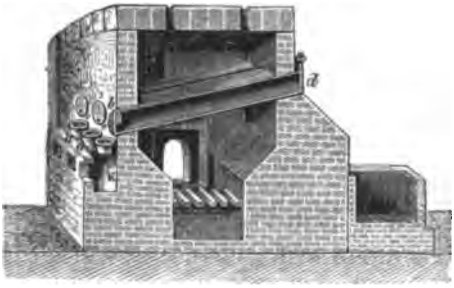

Fig. 11.

Commercial bismuth, however, is still somewhat impure. To free it completely from other metals, it is dissolved in nitric acid, the clear liquid decanted and mixed with water, which throws down a subnitrate of bismuth; and this compound is reduced at a moderate heat, either with black flux, or in a crucible lined with charcoal.

Bismuth crystallises in octohedrons and cubes. It may be obtained in very beautiful crystals, by fusing several pounds of the ordinary metal in a crucible or iron ladle, adding nitre from time to time, and stirring, till a portion of the fused metal, taken out and exposed to the air, no longer assumes an indigo colour, changing to violet or rose and disappearing on cooling, but a fine green or golden tint, which it retains on cooling; then leaving the metal to cool slowly, on a hot sand-bath, for instance, till a crust forms on the surface; piercing this crust with a hot coal; and pouring out the portion which still remains liquid. On subsequently detaching the crust, the inner surface of the metal is found to be covered with beautiful fretted cubes, like those of common salt.

Bismuth is moderately hard, slightly sonorous, and brittle, but may be somewhat extended by careful hammering. Its colour is reddish tin-white, with moderate lustre. The specific gravity of pure bismuth is 9·6542 (Karsten), 9·799 (Marchand and Scherer); of commercial bismuth, 9·822 (Brisson), 9·833 (Herapath), 0·861 (Bergman). Strong pressure rather diminishes than increases the density. Bismuth melts at 480° (Crichton); at 507° (Rudberg); at 509° (Hermann); and expands in solidifying. It boils at an incipient white heat, and if the air be excluded, sublimes in laminæ.

Bismuth forms four compounds with oxygen, viz., the bioxide, BiO_2; the teroxide, BiO_3; the quadroxide BiO_4; and bismuthic acid, BiO_5.

Bioxide or *suboxide of bismuth.*—Bismuth oxidises slowly when exposed to the air at ordinary temperatures, becoming covered with a brownish film of suboxide. When heated in the air till it fuses, it oxidates more rapidly, becoming covered with the same brown oxide, which is renewed as often as it is removed, till the whole of the metal is oxidised. This suboxide is also formed when subnitrate of bismuth is heated with protochloride of tin. By pouring a hydrochloric acid solution of equivalent quantities of teroxide of bismuth and protochloride of tin into excess of moderately strong potash, a black-brown precipitate is formed, consisting of a lower oxide of bismuth combined with stannic acid; and on treating this compound with stronger potash, the stannic acid dissolves and an oxide of bismuth remains, which, when dried in vacuo, or at 100°, out of contact with the air, forms a blackish-grey crystalline powder, consisting of BiO_2, retaining, however, a small quantity of water. It shows but little disposition to absorb oxygen at ordinary temperatures, but when heated, it is instantly converted, with a glimmering light, into teroxide. Acids decompose it into metallic bismuth and teroxide. When ignited in an atmosphere of carbonic acid, it becomes perfectly anhydrous, and in that state does not undergo any perceptible alteration by exposure to the air at ordinary temperatures, and oxidises but slowly even at a red heat (R. Schneider).*

Teroxide of Bismuth, BiO_3; 237 or 3662·5. — Bismuth heated in the air till it boils, takes fire and burns with a faint bluish white flame, forming teroxide of bismuth, the vapour of which condenses on the surface of cold bodies in the form of *flowers of bismuth*. The same oxide is obtained in solution by acting on bismuth with nitric acid, the metal being then dissolved with evolution of nitrous fumes. Strong sulphuric acid likewise dissolves it at a boiling heat, with evolution of sulphurous acid. Hydrochloric acid acts but slightly on it, even with the aid of heat. When the solution of the nitrate is mixed with water, a white precipitate of subnitrate is produced; and this, when gently ignited, yields the teroxide in the form of a lemon-yellow powder. By fusing the hydrated oxide with hydrate of potash, or boiling it with potash-ley, the anhydrous oxide may be obtained in yellow shining needles. Teroxide of bismuth fuses at a strong red heat, and solidifies in a crystalline mass on cooling. It is easily reduced to the metallic state by potassium or sodium at a gentle heat, and by charcoal before the blowpipe.

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* Pogg. Ann. lxxxviii. 45.

Teroxide of bismuth combines with acids, forming salts which are very heavy, colourless, unless the acid itself is coloured, and exert a poisonous action. Heated on charcoal with carbonate of soda, they yield a button of metal. *Zinc, tin, cadmium, iron,* and *lead,* precipitate the metal from the solutions of these salts. *Water* decomposes most bismuth-salts —provided they do not contain too large an excess of acid, throwing down a sparingly soluble basic salt, while the acid remains in solution, together with a small quantity of oxide. *Hydrosulphuric acid* produces a brown-black precipitate of tersulphide of bismuth, insoluble in sulphide of ammonium. *Caustic alkalies,* at ordinary temperatures, throw down the white hydrated oxide, but at a boiling heat, especially if they are concentrated, they produce a yellow precipitate of the anhydrous oxide: these precipitates are insoluble in excess of the alkali. *Alkaline carbonates* throw down a white precipitate of carbonate of bismuth, slightly soluble in excess, but precipitated from the solution by a caustic alkali. *Chromate* or *bichromate of potash* throws down a yellow chromate of bismuth, insoluble in caustic potash, whereby it is distinguished from chromate of lead. Sulphuric acid produces no precipitate.

Quadroxide of bismuth, BiO_4.—When a bismuth-salt contains free chlorine, caustic potash produces in it, not a white but a yellow precipitate, which consists of the hydrate of a higher oxide, but cannot be obtained free from chlorine. When this yellow hydrate is boiled with an alkaline chlorite having a strong alkaline reaction, it turns brown, like peroxide of lead, and is converted into the quadroxide of bismuth (Arppe).

This oxide is completely dissolved by boiling nitric acid; any yellow or green residue that may be left, consists of bismuthic acid. It is perhaps a compound of teroxide of bismuth with bismuthic acid: $BiO_3 \cdot BiO_5$.

Bismuthic acid, BiO_5.—Prepared by passing chlorine through a strong solution of potash in which finely divided teroxide of bismuth is suspended; also, by heating a mixture of potash and teroxide of bismuth for a long time in contact with the air,—or better, by calcining a mixture of teroxide of bismuth, caustic potash, and chlorate of potash. Bismuthic acid, prepared by any of these methods, is always more or less mixed with teroxide of bismuth, which, however, may be dissolved out by weak nitric acid. Bismuthic acid is a light red powder, which, at a temperature a little above 212°, gives off part of its oxygen, and is converted into quadroxide of bismuth. Strong acids also decompose it, reducing it to the state of teroxide of bismuth, which then unites with the acid. Bismuthic acid combines with potash, and forms a few double salts, whose bases are the alkali and teroxide of bismuth.

Bisulphide of bismuth, BiS_2, separates in crystals from a fused mixture of metallic bismuth and the tersulphide, and may also be obtained by fusing 10 parts of bismuth with 3 parts of sulphur, melting the resulting mixture three times with fresh sulphur, and cooling quickly. Hydrochloric acid decomposes this compound, yielding metallic bismuth and the terchloride. Hence, and from the fact that its crystalline form is the same as that of the tersulphide, and that by fusing the tersulphide with metallic bismuth, in certain proportions, crystals may be obtained of the same form but containing less sulphur, Schneider concludes that the supposed bisulphide is merely a mixture of the tersulphide with metallic bismuth.

Tersulphide of bismuth, BiS_3, occurs native as *bismuth-glance*, and may be formed artificially by fusing bismuth with sulphur, and by decomposing bismuth-salts with hydrosulphuric acid. The native variety forms right rhombic prisms, isomorphous with sulphide of antimony: its colour is light lead-grey; specific gravity from 6·4 to 6·5. Tersulphide of bismuth is decomposed by heat; the native sulphide, heated in a tube, yields sublimed sulphur; and the artificial sulphide, when fused and left to cool, yields globules of metallic bismuth as it solidifies.

Selenide of bismuth, $BiSe_3$, is obtained by melting together 1 eq. of bismuth and 3 eq. of selenium, and remelting the product with fresh selenium out of contact with the air. On a recently fractured surface, it exhibits a steel-grey colour, metallic lustre, and a distinct crystalline laminated texture. Its density is 6·82; hardness equal to that of galena: it may be readily pulverised. It is scarcely attacked by hydrochloric acid, but nitric acid and aqua regia decompose it readily (Schneider).

Bichloride of bismuth, $BiCl_2$, is formed by the action of dry hydrogen on the terchloride of bismuth and ammonium, $2NH_4Cl.BiCl_3$, at about 570°, or by heating 1 part of pulverised bismuth with 2 parts of subchloride of mercury in a sealed tube, at about 460°, and purifying the product by repeated fusion in sealed tubes. It is a black hygroscopic mass, which, by heating in the air, and by the action of acids, is resolved into metallic bismuth and the terchloride.

Terchloride of bismuth, $BiCl_3$.—Pulverised bismuth thrown into chlorine gas takes fire and burns with a pale blue light, forming the terchloride. This compound may also be obtained by heating 1 part of bismuth with 2 parts of protochloride of mercury, or by evaporating to dryness the solution of teroxide of bismuth in hydrochloric acid, and distilling the residue out of contact with the air. It is a white opaque solid, with a slight tinge of brown or grey, and a granular fracture; melts very readily, forming an oily liquid. The *hydrated* *terchloride* is obtained in crystals by dissolving the teroxide in hydrochloric acid, and evaporating. The anhydrous chloride, the crystals, and the solution are decomposed by water, yielding *oxychloride of bismuth*, $BiCl_3 . 2BiO_3$, in the form of an insoluble white powder, commonly known as *pearl-white*,—and hydrochloric acid holding a small quantity of bismuth in solution. A *sulphochloride*, of analogous composition, $BiCl_3 . 2BiS_3$, is obtained by heating chloride of bismuth and ammonium with sulphur or tersulphide of bismuth, or by passing hydrosulphuric acid gas over the same compound, heated to a temperature between 485° and 572°, and afterwards heating the product to its melting point in the same gas :—

$$3BiCl_3 + 6HS = BiCl_3 . 2BiS_3 + 6HCl.$$

The product of either of these operations, after being washed, first with water containing so much hydrochloric acid as not to give a precipitate with the terchloride, then with water slightly acidulated, and lastly with pure water, forms small, dark grey, crystalline needles, which, when heated in the air, give off, first, chloride of bismuth, then sulphurous acid, and leave a mixture of oxychloride and basic sulphate of bismuth (Schneider). A *seleniochloride*, $BiCl_3 . 2BiSe_3$, is obtained by adding terselenide of bismuth to fused chloride of bismuth and ammonium. It forms small needle-shaped crystals, having a dark steel-grey colour and metallic lustre (Schneider).

Terchloride of bismuth and ammonium.—A solution of 1 eq. of terchloride of bismuth and 2 eq. of sal-ammoniac, yields, by evaporation, double six-sided pyramids containing $2NH_4Cl . BiCl_3$, isomorphous with the corresponding terchloride of antimony and ammonium (Jacquelain). A solution of 1 eq. terchloride of bismuth and 6 eq. sal-ammoniac yields rhombic crystals, containing $3NH_4Cl . BiCl_3$ (Arppe).

Bismuth dissolves in a boiling solution of protochloride of copper, the liquid being decolorised, and appearing to contain the compound, $3Cu_2Cl . BiCl_3$. Bismuth dissolves in a similar manner in other cupric salts (Schneider).

Teriodide of bismuth, BiI_3.—Obtained as a crystalline sublimate by heating 1 eq. (32 parts) of tersulphide of bismuth with 3 eq. (475 parts) of iodine. Large, thin, crystalline laminæ, having the form of regular six-sided prisms, of a blackish grey colour with a tinge of brown and a strong lustre. The compound, heated in the air, volatilises for the most part, leaving a small quantity of basic oxide of bismuth of a red-brown colour. Boiling water converts it into the same compound. Aqueous potash decomposes it, forming iodate of bismuth, $BiO_3 . 3IO_3$: the same change is more slowly produced by alkaline carbonates. Alkaline sulphides decompose it, forming tersulphide of bismuth. Hydrochloric acid dissolves it without decomposition; nitric acid, with separation of iodine.

Sulphates of bismuth.—When bismuth is heated with strong sulphuric acid, sulphurous acid is evolved, and the metal is converted into a white insoluble powder, consisting of *tersulphate of bismuth*, $BiO_3 . 3SO_3$, which is decomposed by water, yielding a very acid salt which dissolves, and a *monobasic sulphate*, $BiO_3 . SO_3 + HO$, which remains. There is also a *bisulphate of bismuth*, which is obtained in small delicate needles when an acid solution of nitrate of bismuth is mixed with sulphuric acid (Heintz).

Carbonate of bismuth, $BiO_3 . CO_2$, is obtained by adding nitrate of bismuth to the solution of an alkaline carbonate: this salt is used in medicine.

Nitrates of bismuth. — The *neutral* or *ternitrate*, $BiO_3 . 3NO_5 + 10HO$, is obtained by dissolving bismuth in hot nitric acid, evaporating the solution, and leaving it to cool. The salt then separates in transparent oblique prisms of six or eight sides, and terminated with several faces. At 212°

they separate into a solid and a liquid portion, the latter solidifying as it cools. At 302°, they are reduced to the mononitrate, $BiO_3 . NO_5 + HO$; which, when further heated to 500°, gives up all its acid and water, and leaves oxide of bismuth.

Subnitrates of bismuth.—*a.* Ternitrate of bismuth dissolves without decomposition in a small quantity of water, especially if a few drops of nitric acid are added. But a larger quantity of water decomposes it, forming a white precipitate of a subsalt, commonly called *magistery of bismuth.* This substance is generally regarded as a mononitrate containing one atom of water, $BiO_3 . NO_5 + HO$; but, according to Becker*, the basic nitrate obtained directly by treating the ternitrate with cold water, consists of $BiO_3 . NO_5 + 2 HO$. This precipitate, when recently formed, dissolves somewhat freely in water, especially if the water contains nitric acid. Hence, if, after the precipitation of the basic salt, the supernatant liquid be mixed with a large quantity of water, the precipitate is completely redissolved; but after a while, a basic salt separates, containing $5BiO_3 . 4NO_5 + 9Aq$; this, according to Becker, is the true magistery of bismuth, inasmuch as, in the usual mode of preparing that substance, the same change takes place in washing the precipitate. Boiling water decomposes this salt, extracting all the nitric acid, excepting about 1 per cent.—*b.* A salt containing $5BiO_3 . 4NO_5 + 12HO$, is obtained by evaporating a solution of the ternitrate at a strong heat. When the precipitate first obtained by the action of cold water on a solution of the ternitrate is heated in contact with a free acid, or when the same acid solution is poured into hot water, a white, very loose powder is precipitated, containing $6BiO_3 . 5NO_5 + 9HO$. This salt is decomposed by water more readily than the preceding. If it be washed with water as long as the filtrate continues to exhibit a strong acid reaction, a crystalline residue is left on the filter, containing $4BiO_3 . 3NO_5 . 9Aq$. Duflos obtained a *magistery of bismuth* having the same composition, by treating the crystals of the neutral nitrate with 24 times their weight of water. Lastly, if the mononitrate, completely freed from the adhering acid liquid, be treated with water likewise free from acid, it dissolves completely; but the liquid after a while becomes milky, and after long standing deposits a white amorphous powder, containing $5BiO_3 . 3NO_5 + 8HO$. This salt may be formed, in addition to the true magistery of bismuth, if, in the preparation of that substance, too large a quantity of water be used, and the greater part of the acid liquid removed (Becker.) Magistery of bismuth is used as a cosmetic, but has the serious disadvantage of being blackened by hydrosulphuric acid.

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* Archiv. Pharm. lv. 31. and 129.

Bichromate of bismuth, $BiO_3 . 2CrO_3$.—When a solution of ternitrate of bismuth, containing as little free acid as possible, is poured into a moderately concentrated solution of bichromate of potash, bichromate of bismuth is obtained in the form of a yellow flocculent precipitate, which becomes dense and crystalline after a while, or immediately if heated. It may be dried without decomposition between 212° and 257°, but becomes blackish-green at a red heat. It contains 69·48 per cent. of teroxide of bismuth (J. Löwe.)

The *alloys* of bismuth are remarkable for their fusibility. The amalgam of this metal is liquid. An alloy of 8 parts bismuth, 5 lead, and 3 tin, melts at 202°; another mixture of 2 bismuth, 1 lead, and 1 tin, at 200·75°: these mixtures are known by the name of *fusible metal*. Bismuth is also added to the alloy of tin and lead used for casting stereotype plates. Besides increased fusibility, bismuth communicates to this alloy the property of expanding on becoming solid, by which it is rendered capable of taking an accurate impression.

ESTIMATION OF BISMUTH, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

The best reagent for precipitating bismuth from its solutions is carbonate of ammonia; which, when added in excess, throws down the bismuth completely: the liquid must, however, be left to stand for some hours in a warm place, otherwise a considerable quantity of the bismuth will remain in solution. The precipitate, after being washed and dried, must be separated from the filter as completely as possible, the filter separately burned, and the precipitate ignited in a porcelain crucible: a platinum crucible would be attacked by it: after ignition, it consists of teroxide of bismuth containing 89·66 per cent. of the metal.

If the solution contains hydrochloric acid, the bismuth cannot be estimated by precipitation with carbonate of ammonia, or any other alkali, because the precipitate so produced would contain oxychloride of bismuth (p. 255). In this case, therefore, the bismuth must be precipitated by hydrosulphuric acid; the sulphide of bismuth oxidised and dissolved by nitric acid; and the diluted solution treated with carbonate of ammonia, as above.

Bismuth is separated from the *alkalies* and *earths*, and from *iron, cobalt, nickel, zinc,* and *chromium,* by hydrosulphuric acid; from *tin, arsenic,* and *antimony,* by sulphide of ammonium; from *lead,* by sulphuric acid; and from *copper* and *cadmium* by ammonia. The separation of bismuth from cadmium may also be effected by cyanide of potassium, which dissolves the latter as cyanide of cadmium and potassium, and precipitates the bismuth. The precipitated bismuth, however, always contains potash, and must therefore be dissolved in nitric acid and precipitated by carbonate of ammonia. These two metals may also be separated by means of bichromate of potash, which throws down the bismuth as $BiO_3 . 2\,CrO_3$, and retains the cadmium in solution.

ORDER VII.

METALS NOT INCLUDED IN THE FOREGOING CLASSES, WHOSE OXIDES ARE NOT REDUCED BY HEAT ALONE.

SECTION I.

URANIUM.

Eq. 60, *or* 750; U.

THIS metal is obtained from *pitchblende,* a mineral containing from 40 to 95 per cent. of uranoso-uranic oxide, U_3O_4, associated with sulphur, arsenic, lead, iron, and several other metals. The mineral is finely pounded; freed by elutriation from the finer earthy impurities; roasted for a short time, to remove part of the sulphur and arsenic; then dissolved in nitric acid, and the solution evaporated to dryness. The residue is exhausted with water; the solution filtered from the brick-red residue of ferric oxide, ferric arseniate, and lead-sulphate; the greenish yellow filtrate slightly concentrated by evaporation, and left to cool, whereupon it deposits crystals; and the resulting radiated mass of crystallised uranic nitrate drained on a funnel, and then washed with a small quantity of cold water. As the water dissolves a portion of the crystals, it is used in a subsequent operation to redissolve the residue obtained by evaporating the solution of pitchblende in nitric acid. The uranic nitrate, after being dried in the air, is introduced into a wide-mouthed bottle containing ether, in which it immediately dissolves; the yellow solution is left to evaporate in the air; and the resulting crystals are purified by solution in hot water and recrystallisation. The mixed mother-liquids, after dilution with water, are treated with hydrosulphuric acid to precipitate arsenic, lead, and copper, and the filtrate is freed from oxide of iron by evaporating to dryness and digesting the residue in water. The solution thus obtained yields a fresh crop of crystals of uranic nitrate. This salt is converted by ignition into uranoso-uranic oxide, U_3O_4, and from this the protoxide is obtained by ignition with reducing agents (Péligot).

Metallic uranium is obtained by decomposing the protochloride with potassium or sodium. If the mixture be heated in a platinum crucible over a spirit-lamp, and the soluble alkaline chloride washed out by water, the uranium is obtained in the form of a black powder, or sometimes aggregated on the sides of the crucible in small plates, having a silvery lustre and a certain degree of malleability. But, by introducing into a porcelain crucible, first, a layer of sodium, then chloride of potassium, and then a mixture of chloride of potassium and protochloride of uranium (the use of the chloride of potassium being to moderate the action, which is otherwise very violent), placing the porcelain crucible within a closed earthen crucible lined with charcoal, and heating it, first moderately, till the reduction takes place, and then strongly in a blast-furnace for 15 or 20 minutes, the metal is obtained in fused globules (Péligot).

Uranium, in its compact state, is somewhat malleable and hard, but is scratched by steel. Its specific gravity is 18·4; its colour is like that of nickel or iron. When exposed to the air, it soon tarnishes and assumes a yellowish colour. At a red heat it oxidises with vivid incandescence, and becomes covered with a bulky layer of black oxide, which protects the interior from oxidation. In the pulverulent state, it takes fire at about 402°, burning with great splendour, and forming a dark-green oxide. It is permanent in the air at ordinary temperatures, and does not decompose cold water.

It dissolves with evolution of hydrogen in dilute acids, forming green solutions. It combines directly with chlorine, giving out great light and heat, and forming a green volatile chloride. It unites directly with sulphur at a slightly elevated temperature (Péligot).

Uranium forms four compounds with oxygen, viz., the *protoxide*, UO; the *sesquioxide*, U_2O_3; and two intermediate oxides, U_4O_5, and, U_3O_4, which may be regarded as compounds of the other two, viz., $2UO.U_2O_3$ and $UO.U_2O_3$.

Protoxide of uranium; Uranous oxide, UO, 68, or 850.—This oxide is obtained by exposing uranoso-uranic oxide, mixed with charcoal powder, bullock's blood, or oil, to the strongest heat of a blast-furnace; by heating the same oxide to redness in a current of dry hydrogen; by igniting uranic oxalate out of contact of air, or better, in a current of hydrogen; or by igniting the chloride of uranyl and potassium (p. 257), either alone or in a current of hydrogen. Protoxide of uranium has sometimes the form of an earthy powder of a grey or brown colour; sometimes of crystalline scales having the metallic lustre. It was for a long time regarded as metallic uranium,* till Péligot† pointed out its true nature, and obtained the real metal in the manner above mentioned.

Uranous oxide, after ignition, is insoluble in boiling dilute hydrochloric or sulphuric acid, but dissolves in strong sulphuric acid. The hydrated oxide dissolves readily in acids. Solutions of uranous salts are green, and, when treated with alkalies or alkaline carbonates, or with carbonate of lime, yield a reddish-brown gelatinous hydrate of uranous oxide, which dissolves in alkaline carbonates, especially in carbonate of ammonia, forming a green solution. Alkaline hydrosulphates yield a black precipitate of uranous sulphide. Uranous salts are converted into uranic salts by exposure to the air, by the action of nitric acid, and by gold and silver salts; the action in the last case being accompanied by precipitation of metallic gold or silver.

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* See the first edition of this work, page 643.

† Ann. Ch. Phys. [3.], v. 5.; and xii. 258.

Protochloride of uranium; Uranous chloride, UCl, is obtained by burning uranium in chlorine gas, or by passing that gas over an intimate mixture of charcoal and either of the oxides of uranium, strongly heated in a tube of very refractory glass. It crystallises in dark-green regular octohedrons, which have a metallic lustre, and, when heated to redness, volatilise in red vapours and form a sublimate. It fumes strongly on exposure to the air, and dissolves very readily in water, forming a green solution.

Uranous sulphate, $UO.SO_3$, is found native as *uranium-vitriol*, and may be formed artificially by dissolving uranoso-uranic oxide in boiling oil of vitriol; or hydrated uranous oxide in dilute sulphuric acid; or by decomposing a concentrated solution of uranous chloride with sulphuric acid. Crystallises with two and with four atoms of water. A *bibasic uranous sulphate* is obtained by treating the normal salt with a large quantity of water; by exposing the alcoholic solution of that salt to the sun's rays; by careful addition of ammonia to its aqueous solution; and by boiling that solution with green uranoso-uranic oxide. It forms a light-green powder having a silky lustre.

Uranoso-uranic oxide, U_3O_4, or $UO.U_2O_3$.—This oxide forms the principal constituent of pitchblende. It is obtained artificially by burning the metal or the protoxide in the air; by heating the protoxide to redness in an atmosphere of aqueous vapour; and by gentle ignition of uranic oxide or uranic nitrate. It is a dark-green powder which dissolves in acids, forming green solutions, exhibiting characters intermediate between those of uranous and uranic salts, and probably consisting of mere mixtures of the two.

Another intermediate oxide, U_4O_5, or $2UO.U_2O_3$, is said to be formed by strongly igniting the last oxide or the sesquioxide. It is black, and dissolves in acids, like the last; but it is probably a mere mixture of U_3O_4 with the protoxide.

Sesquioxide of uranium; Uranic oxide, U_2O_3; 144, *or* 1800. —Uranium and its lower oxides dissolve in nitric acid, with evolution of nitric oxide and formation of uranic nitrate. When a solution of this salt in absolute alcohol is evaporated at a gentle heat, till nitrous ether begins to escape, an orange-yellow spongy mass is obtained, consisting of hydrated uranic oxide mixed with undecomposed nitrate: the nitrate may be dissolved out by water, and the hydrated oxide then remains, exhibiting a lemon-yellow or orange-yellow colour. This hydrate is permanent in the air, and does not absorb carbonic acid. At 572°, it yields anhydrous uranic oxide, which is also yellow; and at a low red heat, it is converted into green uranoso-uranic oxide.

The *uranic* salts are obtained by oxidising uranous or uranoso-uranic salts with nitric acid, or by exposing them to the air. Most of them contain one equivalent of uranic oxide combined with one equivalent of an acid. Now, as this is contrary to the usual analogy of the normal salts of sesquioxides, most of which contain three equivalents of acid to one equivalent of base, *e.g.*, ferric sulphate $= Fe_2O_3 . 3SO_3$; sulphate of alumina $= Al_2O_3 . 3SO_3$,—Péligot is of opinion that the base of these salts is not really a sesquioxide, but the protoxide of a compound radical *uranyl,* U_2O_2, made up of the elements of 2 equivalents of uranous oxide: $U_2O_3 = (U_2O_2)\,O$. To abbreviate the formulæ, we shall denote the compound radical, uranyl, by the symbol U'; we have then for the formula of uranic sulphate: $U_2O_3 . SO_3 = (U_2O_2)\,O . SO_3 = U'O . SO_3$.

Uranic salts are yellow; they are mostly soluble in water, and, in solution, have a very rough taste, without any metallic after-taste. They are reduced to uranous salts by *hydrosulphuric acid;* also by *alcohol* or *ether,* in sunshine. *Caustic alkalies* added to uranic solutions throw down a yellow precipitate, consisting of a uranate of the alkali, which is insoluble in excess of the reagent. *Alkaline carbonates* produce a yellow precipitate, consisting of a carbonate of uranic oxide and the alkali, soluble in excess, especially in bicarbonate of potash or sesquicarbonate of ammonia. Potash added to these solutions throws down all the uranic oxide. From the solution in carbonate of ammonia, the uranic oxide is likewise precipitated by boiling. *Carbonate of baryta* precipitates uranic oxide completely from its solutions at ordinary temperatures. *Phosphate of soda*, added to uranic salts not containing too much free acid, produces a white precipitate of uranic phosphate, having a slight tinge of yellow. *Sulphide of ammonium* produces a black precipitate of uranic sulphide, which remains for a long time suspended in the liquid. *Hydrosulphuric acid* produces no precipitate. *Ferrocyanide of potassium* produces a dark red-brown precipitate; *ferricyanide of potassium*, none. Metallic *zinc* does not precipitate uranium in the metallic state from uranic solutions, but, after a long time, produces a yellow precipitate of uranic oxide.

Uranic oxide and its salts, fused with *phosphorus-salt* in the outer blowpipe flame, produce a clear yellow glass which becomes greenish on cooling. In the inner flame, the glass assumes a green colour, becoming still greener when cold. Similar colours with *borax*. The oxides of uranium are not reduced to the metallic state by fusion with carbonate of soda on charcoal. Uranic oxide is used for imparting a delicate yellow tint to glass; the glass thus coloured is called *canary glass*.

Chloride of uranyl, $U_2O_2Cl = U'Cl$.—When dry chlorine gas is passed over uranous oxide at a red heat, the tube becomes filled with an orange-yellow vapour of this compound, which solidifies in a yellow crystalline mass, easily fusible, but not very volatile. Dissolved in water, it forms hydrated chloride of uranyl, or hydrochlorate of uranic oxide:

$$U_2O_2Cl + HO = U_2O_3 \, . \, HCl.$$

Chloride of uranyl and potassium, $KCl . U Cl+2Aq.$, is formed by evaporating an aqueous mixture of uranic chloride and chloride of potassium. By heating the hydrated crystals to 212°, the anhydrous compound is obtained.

Uranic sulphate; sulphate of uranyl.—The monosulphate $V'O . SO_3+3Aq.$ is obtained by dissolving uranoso-uranic oxide in strong sulphuric acid, diluting the solution with water, and oxidising with nitric acid; also by decomposing a solution of uranic nitrate with sulphuric acid, expelling the excess of acid by heat, dissolving the residue in water, evaporating the solution to a syrup, and leaving it to crystallise. Forms small lemon-yellow prisms. According to Berzelius, a *bisulphate* and a *tersulphate* are obtained by dissolving the monosulphate in sulphuric acid; but Péligot denies their existence. A basic sulphate is found native in the form of a yellow powder. The monosulphate forms, with sulphate of potash, a crystalline double salt, whose formula is:

$$KO.SO_3+U_2O_3 . SO_3+2HO=\left.\begin{matrix}K\\U'\end{matrix}\right\}2SO_4+2HO.$$

Uranic nitrate; nitrate of uranyl; $U_2O_3.NO_5=U'O.NO_5$, is formed by treating the metal or either of its oxides with nitric acid. It crystallises in lemon-yellow prisms. The solution of this salt possesses the power of lowering the refrangibility of rays of light which fall upon it, producing the peculiar phenomenon called *fluorescence*. This property is likewise exhibited by other compounds of uranium, especially by *canary-glass*. A *basic* nitrate is formed by gently igniting the normal salt.

Uranic phosphates; phosphates of uranyl.—Three of these salts are known, all containing 3 atoms of base to 1 atom of acid. When uranic oxide is digested in a small quantity of aqueous phosphoric acid, a yellow saline mass is produced, part of which dissolves in boiling water, leaving a light yellow powder, which is the *neutral phosphate* $(2U'O . HO) . PO_5$. The aqueous solution concentrated by heat, and then left to evaporate in vacuo over oil of vitriol, deposits a lemon-yellow crystalline salt, consisting of the *acid phosphate* $(U'O . 2HO) . PO_5$. The *basic phosphate* has not been obtained in the separate state; but when uranic nitrate is mixed with a moderate excess of basic phosphate of soda $(3NaO . PO_5)$, a dark yellow precipitate is formed containing $(NaO . 2U'O) . PO_5 + 3U'O . PO_5$ (Wertheim).* When uranic acetate is added to a solution of any soluble phosphate containing an abundance of ammonia and free acetic acid, a yellow precipitate is formed consisting of *ammonio-uranic phosphate,* $2U'O . NH_4O . PO_5$, which, when ignited, leaves uranic pyrophosphate, $2U'O . PO_5$. This reaction affords a ready and exact method of estimating phosphoric acid. The insoluble phosphates, even those of alumina and sesquioxide of iron, are also decomposed by boiling with uranic acetate in presence of a large excess of acetate of ammonia and free acetic acid, the bases dissolving, while the phosphoric remains undissolved in the form of the ammonio-uranic phosphate above described. To separate phosphoric acid from iron in this manner requires, however, a very large excess of the uranium-salt (W. Knop).†

A neutral and an acid *arseniate of uranyl,* analogous in composition to the phosphates, have also been obtained by similar means. The composition of these phosphates and arseniates affords a strong argument in favour of the uranyl theory.

Compounds of uranic oxide with bases. — Uranic oxide combines as an acid with the alkalies, earths, and other metallic oxides, forming salts which may be called *uranates.* The uranates of the alkalies are obtained by precipitating a solution of uranic oxide in an acid with an alkali; the uranates of the earths and heavy metallic oxides, by adding ammonia to a solution of an uranic salt mixed with one of these bases. The uranates are for the most part yellow, and after ignition orange-yellow. The soda-compound, $NaO . 2U_2O_3 + 6HO$, is used for colouring glass, and is prepared on the large scale by roasting pitchblende with limestone in a reverberatory furnace; treating the resulting uranate of lime with dilute sulphuric acid, by which the uranic oxide is almost completely dissolved; mixing the green solution with crude carbonate of soda, by which the uranium is precipitated together with other metals, but redissolved tolerably free from impurities by excess of the alkali; and treating the liquid with dilute sulphuric acid as long as effervescence is produced. The uranate of soda is then precipitated in a form well adapted for the manufacture of yellow glass.

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* J. pr. Chem. xliii. 321.

† Chem. Gaz. 1856, 467.

ESTIMATION OF URANIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Uranium is completely precipitated from uranic solutions by ammonia. The precipitate, which consists of hydrated uranic oxide containing ammonia, must be washed with water containing sal-ammoniac, as it runs through the filter when washed with pure water. It is then dried and ignited in an open crucible, whereby it is converted into uranoso-uranic oxide, U_3O_4; but to obtain a perfectly definite result, and prevent further oxidation during cooling, it is necessary to put the cover on the crucible while the substance is still red-hot, and keep it there till the crucible is quite cold. The oxide thus obtained contains 84·90 per cent. of uranium. An accurate result is likewise obtained by igniting the sesquioxide in an atmosphere of hydrogen, whereby it is reduced to protoxide containing 88·24 per cent. of the metal.

If the uranic solution contains a considerable quantity of an earth or a fixed alkali, the precipitate formed by ammonia carries down with it a certain portion of the earth or alkali;

to free it from which it must, before ignition, be redissolved in hydrochloric acid and reprecipitated by ammonia.

From the *fixed alkalies*, uranium, in the state of sesquioxide, is separated by ammonia, attention being paid to the precaution just mentioned.

From *baryta* it is separated by sulphuric acid; from *strontia* and *lime*, also by sulphuric acid with addition of alcohol.

From *magnesia, manganese, cobalt, nickel, and zinc*, these metals being in the state of protoxide, and the uranium in the state of sesquioxide, it is separated by precipitation with carbonate of baryta.

From *iron* it is separated by carbonate of ammonia, both metals being in the state of sesquioxide; the uranic oxide then dissolves, while the ferric oxide remains undissolved. Care must, however, be taken that the carbonate of ammonia be really monocarbonate, quite free from excess of carbonic acid, otherwise the iron will also be dissolved. To ensure this condition, the carbonate of ammonia must be previously boiled, and the solution of the oxides, if acid, must be neutralised with ammonia till a slight permanent precipitate begins to form: the solution should then be diluted with water. The uranic oxide is separated from the filtrate either by boiling, or by supersaturation with hydrochloric acid and precipitation by ammonia.

From *alumina*, uranium is also separated by carbonate of ammonia, and with greater facility.

From *cadmium, copper, lead, tin, arsenic, antimony*, and *bismuth*, uranium is separated by hydrosulphuric acid; from *titanium* and *chromium* in the same manner as iron is separated from those metals (pp. 152. 171.); and from *vanadium, tungsten, molybdenum*, and *tellurium*, by sulphide of ammonium, in which the sulphides of the last named metals are soluble.

SECTION II.

CERIUM.

Eq. 47·26, *or* 590·87. Ce.

This metal, which was discovered in 1803, simultaneously by Klaproth, and by Hisinger and Berzelius, exists, together with lanthanum and didymium, in cerite, allanite, orthite, yttro-cerite, and a few other minerals, all of somewhat rare occurrence. The most abundant of them is cerite, which is a compound of silicic acid with the oxides of cerium, lanthanum, and didymium, together with small quantities of lime and oxide of iron. To extract the oxides of the three metals, the cerite is finely pounded and boiled for some hours with strong hydrochloric acid, or aqua-regia, which dissolves the metallic oxides, leaving nothing but silica. The filtered solution is then treated with a slight excess of ammonia, which precipitates everything but the lime; the precipitate is redissolved in hydrochloric acid, and the solution treated with excess of oxalic acid. A white or faintly rose-coloured precipitate is then obtained, consisting of the oxalates of cerium, lanthanum, and didymium: it is curdy at first, but in a few minutes becomes crystalline, and easily settles down. When dried and ignited, it yields a red-brown powder, containing the three metals in the state of oxide. The finely pounded cerite may also be mixed with strong sulphuric acid to the consistence of a thick paste, the mixture gently heated till it is converted into a dry white powder, and this powder heated somewhat below redness in an earthen crucible. The three metals are thus brought to the state of basic sulphates, which dissolve completely when very gradually added to cold water; and the solution treated with oxalic acid yields a precipitate of the mixed oxalates, which may be ignited as before.

From the red-brown mixture of the oxides of cerium, lanthanum, and didymium thus obtained, a pure oxide of cerium may be prepared by either of the following processes:—1. The mixed oxides are heated with strong hydrochloric acid, which dissolves the whole, with evolution of chlorine; the solution precipitated with excess of caustic potash; and chlorine gas passed through the liquid with the precipitate suspended in it. The cerium is thereby brought to the state of sesquioxide, which is left undissolved in the form of a bright yellow precipitate, while the lanthanum and didymium remain in the state of protoxides, and dissolve. To ensure complete separation, the passage of the chlorine must be continued till the liquid is completely saturated with it, and the solution, together with the precipitate, left for several hours in a stoppered bottle, and agitated now and then. The liquid is then filtered, the washed precipitate treated with strong boiling hydrochloric acid, which dissolves it with evolution of chlorine, and forms a colourless solution of protochloride of cerium; and this, when treated with oxalic acid or oxalate of ammonia, yields a perfectly white precipitate of oxalate of cerium, which may be converted into oxide by ignition (Mosander). 2. The red-brown mixture of the three oxides is treated with very dilute nitric acid (1 part of nitric acid of ordinary strength to between 50 and 100 parts of water), which dissolves the greater part of the oxides of lanthanum and didymium, and leaves the oxide of cerium; and by treating the residue with very strong nitric acid, the last traces of lanthanum and didymium may be extracted (Mosander, Marignac). 3. The red-brown mixture of the three oxides is boiled for several hours in a strong solution of chloride of ammonium. The oxides of lanthanum and didymium then dissolve, with evolution of ammonia, and ceric or ceroso-ceric oxide is left in a state of purity. It must be collected on a filter and washed with a solution of sal-ammoniac, because, when washed with pure water, it first runs through the filter, and then stops it up (Watts).*

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* Chem. Soc. Qu. J. ii. 147.

Metallic cerium is obtained by heating the pure anhydrous protochloride with potassium or sodium. It is a grey powder which acquires the metallic lustre by pressure. It oxidises readily, decomposes water slowly at ordinary temperatures, quickly at the boiling heat, and dissolves rapidly in dilute acids, with evolution of hydrogen, forming a solution of a cerous salt.

Protoxide of cerium; Cerous oxide, CeO; 55·26 or 690·8.—This oxide is scarcely known in the anhydrous state. The sesquioxide, exposed to the strongest heat of a wind-furnace, in a crucible lined with charcoal, yields a residue chiefly consisting of protoxide, but the reduction is never complete. The hydrated protoxide is easily obtained by precipitating the chloride with a caustic alkali. It dissolves readily in acids, forming the *protosalts of cerium* or *cerous salts*, the solutions of which are distinguished by the following characters: *Caustic potash* or *soda* produces a white precipitate of the hydrated protoxide, which is insoluble in excess, and is converted into the yellow sesquioxide by the action of chlorine or hypochlorous acid. *Ammonia* precipitates a basic salt. *Alkaline carbonates* form a white precipitate of cerous carbonate insoluble in excess. *Oxalic acid* or *oxalate of ammonia* produces a white precipitate of cerous oxalate, gelatinous at first, but quickly assuming the crystalline character, and converted by ignition in an open vessel into a salmon-coloured powder, consisting of sesquioxide of cerium mixed with protoxide. Hydrosulphuric acid produces no precipitate. *Sulphide of ammonium* throws down the hydrated protoxide. *Ferrocyanide of potassium* produces a white pulverulent precipitate; ferricyanide of potassium, none. *Sulphate of potash* produces a white crystalline precipitate of potassio-cerous sulphate, nearly insoluble in pure water, and quite insoluble in excess of sulphate of potash. With dilute solutions the precipitate takes some time to form. This character, together with the behaviour of the oxalate, and the yellow coloration of the hydrated protoxide by chlorine, serves to distinguish cerium from all other metals. Cerous salts in solution have a sweet astringent taste, and redden litmus, even when the acid is perfectly saturated. All compounds of cerium, ignited with *borax* or *phosphorus-salt* in the outer blowpipe-flame, yield a glass which is deep red while hot, but becomes colourless on cooling. In the inner flame a colourless bead is formed, but when ignited with excess of oxide of cerium, it forms a yellow enamel.

Sesquioxide of cerium; Ceric oxide, Ce_2O_3.—It is doubtful whether this oxide has been obtained in the separate state. The hydrated protoxide, the nitrate, and the oxalate, yield, when ignited in the acid, a salmon-coloured powder, which is generally regarded as ceric oxide; but, according to Marignac, it is a mixture or compound of the sesquioxide and protoxide of cerium, not quite constant in composition, but containing on the average 82·15 per cent of metal, and therefore nearly agreeing with the formula Ce_7O_9 or $3CeO.2Ce_2O_3$. When mixed with oxide of didymium, its colour is red-brown. This oxide is nearly insoluble in strong nitric and hydrochloric acids, even at the boiling heat, but strong boiling sulphuric acid dissolves it. Hydrochloric acid, with the aid of reducing agents, such as alcohol, dissolves it slowly at the boiling heat, forming a solution of cerous chloride. If mixed with the oxide of lanthanum or didymium, it dissolves readily in strong boiling hydrochloric acid, with evolution of chlorine. The solution of this oxide in strong sulphuric acid has a bright yellow colour, and deposits yellow prismatic crystals, which, according to Marignac, consist of a *ceroso-ceric-sulphate*, containing $Ce_7O_9 . 4SO_3 + 7HO$. Potash, added to the solution of this salt, throws down a yellow hydrate, which dissolves readily in acids. The solutions are yellow, and, when boiled with hydrochloric acid, are converted into cerous salts.

Protosulphide of cerium, CeS, is obtained by igniting the carbonate in vapour of bisulphide of carbon, or by heating an oxide of cerium with sulphide of potassium. The first process yields a light powder of the colour of red lead; the second, a product resembling mosaic gold. The *sesquisulphide of cerium* is not known in the free state, but exists in certain sulphur-salts.

Protochloride of cerium, CeCl. — Cerium burns vividly when heated in chlorine gas, and forms this compound. The anhydrous chloride may be prepared by igniting the sulphide, or the residue obtained by evaporating to dryness a solution of the chloride mixed with sal-ammoniac, in a current of chlorine gas. If the air is not completely excluded, an oxychloride is also produced. The anhydrous chloride is a white porous mass, fusible at a red heat, and perfectly soluble in water. A *hydrated chloride* is obtained in colourless four-sided prisms, by dissolving the hydrated oxide or the carbonate in hydrochloric acid, and evaporating to a syrup. The solution, when exposed to the air, turns yellow, from formation of a ceric salt.

Sesquichloride of cerium.—The hydrated sesquioxide dissolves in cold hydrochloric acid, forming a red solution, which, however, soon gives off chlorine, and is reduced, more or less completely, to protochloride.

Protofluoride of cerium is formed by precipitating the protochloride with an alkaline fluoride. The *sesquifluoride* occurs native in six-sided prisms, mixed with half its weight of protofluoride; also with the fluorides of yttrium and calcium, in *yttrocerite*. An oxyfluoride of cerium, $Ce_4F_3O_3+3HO$, is also found native.

Cerous carbonate, $CeO \, . \, CO_2+3HO$, is formed by exposing the hydrated protoxide to the air, or by precipitation.

Cerous oxalate, $C_4Ce_2O_8$, is precipitated from cerous salts by oxalic acid or oxalate of ammonia added in excess, even when the solution contains a considerable quantity of free nitric or hydrochloric acid. It is at first curdy, but soon becomes very dense and crystalline. When ignited with free access of air, it yields ceroso-ceric oxide.

Cerous sulphate, $CeO \cdot SO_3$.—The anhydrous salt is a white powder, which, when sprinkled with a small quantity of water, becomes very hot, and condenses into a solid mass, very difficult to dissolve. It forms two crystalline hydrates, viz., $2(CeO \cdot SO_3)+3HO$ and $(CeO \cdot SO_3)+3HO$. The anhydrous salt, heated in a close vessel, leaves a basic cerous sulphate; but, with free contact of air, it leaves a basic ceric or ceroso-ceric sulphate. Cerous sulphate forms with sulphate of potash a crystalline double salt, containing $CeO \cdot SO_3+KO \cdot SO_3$, which is nearly insoluble in water.

Cerous phosphate.—Obtained by precipitating a cerous salt with phosphate of soda. It also occurs native (associated with the phosphates of lanthanum and didymium), in several forms. In *Monazite* and *Edwardsite*, it occurs in oblique rhombic prisms; in the former it is associated with thorina, and small quantities of lime, manganese, and tin; in the latter, with alumina, zirconia, and silica. *Cryptolite* is a tribasic phosphate of cerium, occurring in the rose-coloured apatite of Arendal in Norway, and is separated by dissolving the apatite in nitric acid. It then remains in the form of a crystalline powder, appearing under the microscope to consist of hexagonal prisms. Sp. gr. 4·6 (Wöhler).* *Phosphocerite* is a mineral similar in composition to cryptolite. It was discovered by Mr. O. Sims in the cobalt-ore of Johannisberg in Sweden, of which it forms about one-thousandth part. It remains as a residual product when the ore after calcination is treated with hydrochloric acid for the purpose of extracting the cobalt. It is a greyish yellow crystalline powder, mixed with a small quantity of minute dark purple crystals, which are strongly attracted by the magnet, and consist chiefly of magnetic oxide of iron. The crystals of phosphocerite, when examined by the microscope, exhibit two forms, one an octohedron, the other, a four-sided prism with quadrilateral summits, both forms apparently belonging to the right prismatic system. Sp. gr. 4·78. The mineral contains 64·68 per cent. protoxide of cerium, &c., 28·46 phosphoric acid, 2·83 oxide of iron, and 3·41 oxide of cobalt, silica, &c. It is very rich in didymium. Strong sulphuric acid, aided by gentle heat, decomposes it, forming a pasty mass, which dissolves in cold water with the exception of a small quantity of silica (Watts).*

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* Ann. Ch. Pharm. lvii. 268.

ESTIMATION OF CERIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Cerium is precipitated from neutral solutions of cerous salts by potash, as cerous hydrate; or by oxalate of ammonia, as cerous oxalate; and either of these compounds is converted by ignition in an open vessel into ceroso-ceric oxide. This oxide, as already observed, is not perfectly definite in constitution; it may be stated approximately to contain 96·5 per cent. of cerous oxide, or 82·5 per cent. of the metal, and this estimate may be adopted where great accuracy is not required. A more exact method, however, is to dissolve the hydrate precipitated by potash in dilute sulphuric acid, then evaporate, and heat the residue to commencing redness, whereby it is converted into the anhydrous sulphate $CeO . SO_3$, containing 57·6 per cent. of the protoxide of cerium, or 49·6 per cent. of the metal.

Hydrosulphuric acid serves to separate cerium from all metals which are precipitated by that reagent from their acid solutions.

From *manganese, iron, cobalt, nickel, zinc, titanium, chromium, vanadium,* and *tungsten,* cerium may be separated by means of a saturated solution of sulphate of potash.

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* Chem. Soc. Qu. J., ii. 131.

From *alumina* it may be separated by carbonate of baryta, which precipitates alumina and not cerous oxide; from *glucina* by sulphate of potash.

From *yttria*, with which it is often associated in minerals, it is separated by a saturated solution of sulphate of potash added in excess, the sulphate of yttria and potash being soluble in excess of sulphate of potash, while the cerous double salt remains undissolved.

From *zirconia*, cerium is separated by treating the boiling acid solution with sulphate of potash, whereby the greater part of the zirconia is precipitated as basic sulphate, while the cerium remains dissolved; to complete the precipitation, a small quantity of ammonia must be added, but not sufficient to saturate the acid (H. Rose).

From *magnesia* also cerium may be separated by sulphate of potash; from *baryta*, *strontia*, and *lime*, it is separated by ammonia added in slight excess; or from baryta by sulphuric acid, and from strontia and lime by sulphuric acid and alcohol; and from the *fixed alkalies* by precipitation with oxalate of ammonia.

SECTION VI.

LANTHANUM.

Eq. 47, *or* 588; La.

The red-brown oxide obtained from cerite by the methods already described (p. 261), and originally regarded as the oxide of a single metal, cerium, was shown by Mosander*, in 1839, to contain the oxide of another metal, to which he gave the name *lanthanum*. Subsequently, in 1841 †, Mosander discovered that even this supposed simple oxide contained two distinct metals, for one of which the name of lanthanum was retained, while the other was called *didymium*. These two metals appear to be constantly associated with cerium, though not always in the same proportion.

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* Pogg. Ann. xlvi. 648; xlvii. 207.

† Ibid. lvi. 504.

The separation of lanthanum and didymium from cerium may be effected by either of the methods already described (p. 262); the second and third are easier and more expeditious than the first. If the solution obtained by treating the crude red-brown oxide with dilute nitric acid be evaporated to dryness, and the residue treated with nitric acid diluted with at least 200 parts of water, a solution will be obtained quite free from cerium (Marignac). Boiling the red-brown oxide with chloride of ammonium also yields a solution of lanthanum and didymium free from cerium. In both cases, however, it is best to test a portion of the solution for cerium by precipitating with excess of caustic potash, and passing chlorine through the solution. The presence of cerium, even in very small quantity, will be indicated by the formation of a yellow precipitate, after the liquid, supersaturated with chlorine, has been left in a close vessel for several hours.

A solution free from cerium having been obtained, the separation of the lanthanum and didymium is effected by the different solubilities of their sulphates. To convert them into sulphates, the solution is treated with excess of a caustic alkali, and the washed precipitate dissolved in dilute sulphuric acid. The mode of proceeding varies according as the lanthanum or the didymium is in excess.

1. When the lanthanum is in excess, in which case the solution has but a faint amethyst tinge, the liquid is evaporated to dryness, and the residue heated in a platinum-dish to a temperature just below redness, to drive off the excess of acid, and render the sulphates perfectly anhydrous. The residue is then dissolved in rather less than six times its weight of water, at about 36° Fah. (2° or 3° C.), the salt being reduced to powder and added in successive small portions,

and the vessel containing the liquid being immersed in ice-cold water. Without these precautions, the temperature of the liquid may be raised several degrees, in consequence of the heat evolved by the combination of the anhydrous sulphates with water; and, in that case, crystallisation will commence, and rapidly extend through the whole mass of liquid, as these sulphates are much less soluble in warm than in cold water; but if the liquid be properly cooled, the whole dissolves completely. The solution is next to be heated in the water-bath to about 104° F. (40° C.); the sulphate of lanthanum then crystallises out, accompanied by only a small quantity of sulphate of didymium. To purify it completely, it is again rendered anhydrous, redissolved in ice-cold water, &c., and the entire process repeated ten or twelve times. The test of purity is perfect whiteness, the smallest quantity of didymium imparting an amethyst tinge (Mosander).

2. When the didymium-salt is in excess, in which case the liquid has a decided rose-colour, separation may be effected by leaving the solution containing excess of acid, in a warm place for a day or two. The sulphate of didymium then separates in large rhombohedral crystals modified with numerous secondary faces; and, at the same time, slender, needle-shaped, violet-coloured crystals are formed, containing the two sulphates mixed. The rhombohedral crystals, which are nearly free from lanthanum, are removed, and the needles, together with the mother-liquid, treated as in the first method, to obtain sulphate of lanthanum (Mosander).

In both cases, the separation may be greatly facilitated by first dissolving the mixed oxides of the two metals in a large excess of nitric acid, and precipitating in successive portions by oxalic acid: the first precipitates thus formed have a much deeper rose-colour, and are much richer in didymium than the latter. The separation thus effected is very imperfect in itself, but it greatly facilitates the subsequent separation of the sulphates, which is much more rapid, when one of the sulphates is in great excess with regard to the other (Marignac).

Metallic lanthanum is obtained by decomposing the anhydrous chloride with sodium, and dissolving out the chloride of sodium with alcohol of sp. gr. 0·833. It is a dark, lead-grey powder, soft to the touch, and adhering when pressed.

Protoxide of lanthanum, LaO, 55 or 688, is obtained in the anhydrous state by igniting the precipitated hydrate or carbonate in a covered crucible. It is a white powder, which turns brown when heated in the air, probably from partial conversion into a higher oxide. The *hydrated oxide* is formed when the metal or the anhydrous oxide is immersed in warm water, or when a salt of lanthanum is precipitated by caustic potash. It is a white substance, viscid while moist, and slightly alkaline to test-paper. It absorbs carbonic acid from the air with great rapidity.

Oxide of lanthanum, even after strong ignition, dissolves very easily in acids. When boiled with a solution of chloride of ammonium, it dissolves and expels the ammonia. The salts of lanthanum are perfectly colourless when free from didymium. The soluble salts have an astringent taste. *Potash* and *soda*, added to the solutions, throw down the hydrated oxide, which dissolves completely in chlorine-water, without forming any yellow deposit. *Ammonia* throws down a basic salt. *Oxalic acid* or *oxalate of ammonia*, throws down a white flocculent precipitate, which does not become crystalline. In other respects, the solutions resemble those of cerous salts. Compounds of lanthanum do not impart any colour to borax or phosphorus-salt.

Chloride of lanthanum is obtained in the anhydrous state by igniting the oxide in a current of hydrochloric acid gas, and as a hydrate by evaporating a solution of the oxide in hydrochloric acid. It dissolves very readily in water.

Carbonate of lanthanum is found native in small crystalline scales, containing traces of protoxide of cerium. When obtained by precipitation, it forms a gelatinous mass, which gradually changes into shining crystalline scales (Mosander).

Sulphate of lanthanum, $LaO . SO_3$, is obtained by spontaneous evaporation in small prismatic crystals, containing 3 eq. of water of crystallisation. It parts with its water at a low red heat, and with half its acid at a strong red heat. It is much less soluble in hot than in cold water (p. 272). It forms with sulphate of potash a very sparingly soluble double salt, similar to the sulphate of cerium and potassium.

Nitrate of lanthanum crystallises in deliquescent colourless prisms, very easily soluble in water and in alcohol. When carefully heated, so as not to expel any of the acid, it fuses, and solidifies into a colourless glass on cooling. If the heat is raised, so as to drive off a portion of the acid, a fused mass remains which, on cooling, forms a kind of enamel, but almost immediately afterwards crumbles to a bulky white powder, and with such force that the particles are scattered about to a considerable distance (Mosander).

ESTIMATION OF LANTHANUM.

Lanthanum is precipitated from its solutions by potash, or by oxalate of ammonia, and the precipitate converted by ignition in a covered platinum crucible into the anhydrous oxide, containing 85·7 per cent. of the metal.

The methods of separating lanthanum from other metals are the same as those adopted for cerium. The separation of lanthanum from cerium itself may be effected by boiling the mixed oxides in a solution of chloride of ammonium (p. 262).

SECTION VII.

DIDYMIUM.

Eq. 48 *or* 600; Di.

Didymium was discovered by Mosander in 1841*; and its compounds have since been more minutely examined by Marignac.†

A pure salt of didymium is obtained by recrystallising the rose-coloured rhombohedrons which separate from an acid solution of the mixed sulphates of lanthanum and didymium by spontaneous evaporation; and from the pure sulphate thus prepared, the other compounds of the metal may be formed.

Metallic didymium is obtained by heating potassium with an excess of chloride of didymium, and washing out the soluble chlorides with cold water. It is thus obtained, for the most part, as a grey metallic powder; but partly, also, in fused globules. The powder, thrown into the flame of a spirit-lamp, burns with bright sparks like iron-filings. The powder decomposes water at ordinary temperatures; the fused granules do not: in either form, however, the metal dissolves rapidly in dilute acids, with evolution of hydrogen.

Protoxide of didymium, DiO, 56 or 700. — Obtained in the anhydrous state by strongly igniting the nitrate, oxalate, or the precipitated hydrate in a covered crucible. It is perfectly white; is slowly converted into a hydrate by immersion in warm water; dissolves readily in the weakest acids; and expels ammonia from ammoniacal salts when boiled with them. The hydrate, DiO.HO, is a gelatinous mass resembling alumina, but having a very pale rose-colour. It contracts much by desiccation.

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* Pogg. Ann. lvi. 504.

† Ann. Ch. Phys. [3], xxxviii. 148; Chem. Soc. Qu. J., vi. 260.

The *salts of didymium* have either a pure rose-colour, like the sulphate, or slightly inclining to violet, like the nitrate in the state of strong solution. *Potash, soda,* and *ammonia* precipitate the hydrate; so does *sulphide of ammonium. Carbonate of baryta* also throws down the hydrated oxide slowly, but completely. *Oxalate of ammonia* precipitates didymium completely from neutral solutions; and *oxalic acid* almost completely, unless the solution contains a large excess of acid. The *sulphates of potash, soda,* and *ammonia* form, immediately in strong, and gradually in weak solutions, rose-white precipitates of double sulphates, slightly soluble in water, less soluble in excess of the reagent; the soda-salt is the least soluble of the three. *Phosphoric* and *arsenic acids,* at a boiling heat, form precipitates sparingly soluble in acids. All compounds of didymium impart to *borax* and *phosphorus-salt* a very pale rose-colour. They do not colour carbonate of soda before the blowpipe.

Peroxide of didymium.—When the oxalate, nitrate, carbonate, or hydrate of didymium is ignited in contact with the air, and not very strongly, a dark brown oxide is obtained, containing from 0·32 to 0·88 per cent. of oxygen more than the protoxide. When treated with acids it dissolves readily, giving off the excess of oxygen, and forming a solution containing the protoxide. It is probably a mixture of the protoxide with a small quantity of a higher oxide of definite composition. By strong ignition in a close vessel, it is converted into the white protoxide.

Sulphide of didymium, DiS, is obtained by igniting the oxide in the vapour of bisulphide of carbon. It is a light, brownish green powder, which dissolves in acids, with evolution of hydrosulphuric acid. A greyish-white *oxysulphide,* 2DiO.DiS, is obtained by igniting the oxide with carbonate of soda and excess of sulphur, and digesting the fused mass in water (Marignac).

Chloride of didymium is obtained as a hydrate in rose-coloured crystals of considerable size, by evaporating a solution of the oxide in hydrochloric acid. The crystals, which are very soluble in water and alcohol, contain $DiCl.4HO$. The solution, when evaporated, gives off hydrochloric acid, and leaves an oxychloride, not however of constant composition (Marignac).

Carbonate of didymium, $DiO.CO_2$.—Precipitated as a white, bulky hydrate, tinged with rose-colour, on adding an alkaline carbonate or bicarbonate to a salt of didymium. The precipitate formed in the cold with nitrate of didymium and bicarbonate of ammonia, contains, after drying in *vacuo,* $DiO.Cl_2 + 2HO$. At 212°, it gives off $1\frac{1}{2}$ eq. water and a small quantity of carbonic acid (Marignac).

Oxalate of didymium, $C_4Di_2O_8$, is precipitated from neutral solutions as a rose-white powder, which dissolves in warm nitric or hydrochloric acid, and separates, on cooling, in the form of a granular crystalline powder, sometimes even in small rose-coloured prismatic crystals. After drying in the air, it contains 8 eq. water, 6 eq. of which go off at 212° (Marignac).

Sulphate of didymium, $DiO.SO_3$.—Formed by dissolving the oxide or carbonate in dilute sulphuric acid. The solution is rose-coloured, and deposits, by spontaneous evaporation, dark rose-coloured, shining crystals, having the form of an oblique rhomboidal prism (Mosander), and cleaving readily and distinctly in a direction parallel to the base. They contain $3(DiO.SO_3) + 8\,Aq.$, and give off the whole of their water at 392° F. (200° C.), leaving an anhydrous powder, which may be heated to redness without further alteration. A solution of the sulphate, when heated, especially to the boiling point, deposits a crystalline precipitate containing $DiO.SO_3 + 2HO$. The following table exhibits the solubility of the anhydrous salt, and of the two crystalline hydrates in water at different temperatures:—

Temperature.	Anhydrous Sulphate.	Sulphate with 2 eq. water.	Sulphate crystallised in the cold.
12° C	43·1	—	—
14	39·3	—	—
18	25·8	16·4	—
19	—	—	11·7
25	20·6	—	—
38	13·0	—	—
40	—	—	8·8
50	11·0	—	6·5
100	—	—	1·7

The anhydrous sulphate, exposed to the heat of an intense charcoal fire, gives off two-thirds of its sulphuric acid, and leaves a ***tribasic sulphate***, $3DiO.SO_3$ (Marignac).

Sulphate of didymium, mixed in solution with ***sulphate of potash***, forms a crystalline double salt, which appears to contain $KO.SO_3 + 3(DiO.SO_3) + 2HO$; it dissolves in sixty-three times its weight of cold water. With ***sulphate of soda*** it forms the anhydrous double salt, $NaO.SO_3 + 3(DiO.SO_3)$, which requires two hundred times its weight of water to dissolve it, and is still less soluble in a solution of sulphate of soda. With ***sulphate of ammonia***, it forms the salt $NH_4O.SO_3 + 3(DiO.SO_3) + 8HO$, soluble in eighteen times its weight of water (Marignac).

Sulphite of didymium, $DiO.SO_2 + 2HO$.—Oxide of didymium suspended in water, is readily dissolved by a stream of sulphurous acid gas, forming a rose-coloured solution which becomes turbid when heated, forming a light bulky precipitate, which redissolves as the liquid cools, unless the temperature has been raised to the boiling point, in which case it remains undissolved (Marignac).

Nitrate of didymium, $DiO.NO_5$.—This salt is very soluble in water and in alcohol of the strength of 96 per cent. The aqueous solution has a pure rose colour when dilute, but appears violet by reflected light when strong. A syrupy solution solidifies on cooling into a deliquescent crystalline mass, which, when carefully heated to 300° C., melts, becomes perfectly anhydrous, and exhibits the composition of the neutral nitrate. At a higher temperature, it is decomposed, giving off nitrous fumes, and leaving a residue from which water extracts a portion of neutral nitrate, and leaves a basic salt containing $4DiO.NO_5 + 5HO$. (Marignac).

Phosphate of didymium, $3DiO.PO_5 + 2HO$. — Precipitated, after a few hours, as a white powder, on adding a strong solution of phosphoric acid to a strong solution of nitrate of didymium. It is insoluble in water, very sparingly soluble in dilute acids; but dissolves readily in the stronger acids when concentrated; gives off its water when ignited (Marignac).

Arseniate of didymium, $5DiO.2AsO_5 + 2HO$. — Obtained as a pulverulent precipitate by the action of arsenic acid on solutions of didymium at the boiling heat, or as a gelatinous precipitate by the action of neutral arseniate of potash at ordinary temperatures. It is but slightly soluble in dilute acids (Marignac).

The *quantitative estimation* of didymium is effected in the same manner as that of lanthanum. The anhydrous protoxide contains 85·7 per cent. of the metal.

The methods of separating didymium from the preceding metals are also the same as for lanthanum. For separating it from lanthanum itself, no method has yet been devised sufficiently exact for quantitative analysis.

SECTION VIII.

TANTALUM.

Eq. 68·82 *or* 860·3; Ta.

This metal was discovered by Ekeberg in 1802. It is a rare metal, occurring only in a few minerals, the principal of which are Swedish *tantalite* and *yttro-tantalite*.

Tantalum is obtained, in the metallic state, by heating the fluoride of tantalum and potassium, or fluoride of tantalum and sodium, with sodium, in a well covered iron crucible, and afterwards washing out the soluble salts by water. The reduced metal thus obtained is not quite pure, being more or less contaminated with acid tantalate of soda, the quantity of which may, however, be diminished by covering the mixture in the crucible with chloride of potassium.

Tantalum is a black powder, which, according to H. Rose, is a good conductor of electricity. When heated in the air, it burns with a bright light, and is converted, though with difficulty, into tantalic acid. It is not attacked by sulphuric, hydrochloric, or nitric acid, or even by aqua regia. It dissolves slowly in warm aqueous hydrofluoric acid, with evolution of hydrogen, and very rapidly in a mixture of hydrofluoric and nitric acids.

Tantalum forms two compounds with oxygen, viz., *tantalous acid*, probably TaO, and *tantalic acid*, TaO_2.

Tantalous acid is obtained by placing tantalic acid in a small cavity in a crucible filled with charcoal, and exposing it to the strongest heat of a blast-furnace; a thin film on the outside is at the same time reduced to the state of metal. It is a dark grey mass which scratches glass, and acquires metallic lustre by burnishing.

Tantalic acid, TaO_2; 84·82 or 1060·3.* — This compound is formed when tantalum burns in the air; also by the action of water on chloride of tantalum; and, in the form of a potash-salt, by fusing metallic tantalum or tantalous acid with hydrate, carbonate, or bisulphate of potash. It exists, in combination with various bases, in the minerals above mentioned, and is usually extracted from tantalite, which contains the oxides of iron and manganese, together with small quantities of stannic and tungstic acids, by one of the following processes:—1. The mineral, after being pulverised and levigated, is fused with twice its weight of hydrate of potash; the fused mass digested in hot water; and the filtered solution supersaturated with hydrochloric or nitric acid: hydrated tantalic acid is then precipitated in white flakes, which may be purified by washing with water (Berzelius). 2. A better method, however, is to fuse the levigated tantalite in a platinum crucible with six or eight times its weight of bisulphate of potash; pulverise the mass when cold; and boil it repeatedly with fresh quantities of water till no more sulphate of potash, iron, or manganese is dissolved out of it. The residue, which consists of hydrated tantalic acid mixed with ferric oxide, stannic acid, and tungstic acid, is then digested in sulphide of ammonium containing excess of sulphur, which removes the stannic and tungstic acids, and converts the iron into sulphide; the liquid is filtered, and the tantalic acid washed with water containing sulphide of ammonia, then boiled with strong hydrochloric acid to remove the iron, and finally washed with boiling water. The hydrated tantalic acid thus prepared is converted into the anhydrous acid by ignition. It may still, however, contain silica, to remove which, it is dissolved in aqueous hydrofluoric acid, the filtered solution mixed with sulphuric acid and evaporated to dryness, and the residue ignited as long as its weight continues to diminish: the silica is then expelled as gaseous fluoride of silicon (Berzelius).

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* The composition of tantalic acid is usually represented by the formula TaO_3, which, according to the original analysis of that compound by Berzelius (88·5 per cent. tantalum + 11·5 per cent. oxygen), gives for tantalum the equivalent number 185. But according to the recent experiments of H. Rose (Berl. Akad. Ber. 1856, 385), the tantalum-compounds appear to contain 2 eq. of the chlorous element, viz., the chloride, $TaCl_2$, tantalic acid, TaO_2, &c.; he also finds the chloride to contain 49·25 per cent. of tantalum, making the equivalent of tantalum 68·82.

Anhydrous tantalic acid is a white powder, which remains white when heated, or acquires but a very faint tinge of yellow. Its specific gravity varies from 7·022 to 8·264, increasing with the temperature to which the acid has been exposed (H. Rose). It neither melts nor volatilises when heated, and is destitute of taste and smell. It is reduced to the metallic state in the circuit of a very powerful voltaic battery; partially also by very strong ignition in contact with charcoal. When ignited in the vapour of bisulphide of carbon, it yields sulphide of tantalum:

$$2TaO_2 + 4CS_2 = Ta_2S_3 + 4CO + 5S.$$

It is insoluble in all acids, and can only be rendered soluble by fusion with hydrate or carbonate of potash.

Hydrated tantalic acid, obtained by precipitating an aqueous solution of tantalate of potash with hydrochloric acid, or by decomposing chloride of tantalum with water containing a small quantity of ammonia, is a snow-white bulky powder, which reddens litmus-paper while moist, and dissolves in hydrochloric and hydrofluoric acids. When strongly heated it gives off its water and becomes incandescent. The hydrate, obtained by fusing tantalite with bisulphate of potash in the manner above described, is of a denser and more crystalline character, is insoluble in all acids excepting strong sulphuric acid, and is precipitated from the solution by water. When heated, it becomes anhydrous, but does not emit light.

Tantalic acid combines with *bases* much more readily than with acids. When fused with *hydrate of potash* in a silver crucible, it forms a transparent mass of tantalate of potash, which, after cooling, dissolves completely in water. With *hydrate of soda* it fuses into an opaque turbid mass, and ultimately deposits a sediment, which is not taken up by fusion with any excess of the alkali. Water poured upon the fused mass when cold dissolves out the excess of soda, but not a trace of tantalic acid; and the residue, when treated with fresh water, dissolves and forms an opalescent solution of acid tantalate of soda, which salt is completely insoluble in a strong solution of caustic soda, and is therefore precipitated on mixing the liquid with the solution of soda previously obtained by treating the fused mass with water. When tantalic acid is fused with *carbonate of potash* or *soda*, the fused mass is not completely soluble in water.

Hydrochloric acid, added in excess to the solution of an alkaline tantalate, first precipitates the tantalic acid, and then redissolves it, forming a slightly opalescent liquid. *Sulphuric acid* also precipitates the tantalic acid, but does not redissolve it when added in excess. *Carbonic acid gas*, passed through the solution of an alkaline tantalate, precipitates the whole of the tantalic acid in the form of an acid salt. *Chloride* or *sulphate of ammonium* also precipitates the tantalic acid from these solutions in the form of hydrate, mixed with small quantities of ammonia and the fixed alkali. The presence of carbonate of potash or soda prevents the formation of this precipitate at ordinary temperatures; but it then appears after boiling for some time. Sulphide of ammonium produces no precipitate. *Chloride of barium* or *calcium* forms a precipitate of tantalate of baryta or lime, insoluble in water and in ammoniacal salts. *Nitrate of silver* forms, in the solution of a neutral alkaline tantalate, a white precipitate, which is turned brown by a small quantity of ammonia, and dissolves in a larger quantity. A solution of *basic mercurous nitrate* forms a yellowish white precipitate, which turns black when heated. *Ferrocyanide of potassium*, added to a very slightly acidulated solution of an alkaline tantalate, forms a yellow precipitate; *ferricyanide of potassium* a white precipitate. *Infusion of galls*, added to a solution of an alkaline tantalate acidulated with sulphuric or hydrochloric acid, forms a light yellow precipitate soluble in alkalies. *Zinc*, immersed in the solution of an alkaline tantalate acidulated with hydrochloric acid, does not produce any blue colour; neither is that colour produced, or but very faintly, on addition of sulphuric acid. But if chloride of tantalum be dissolved in strong sulphuric acid, and then water and metallic zinc added, a fine blue colour is produced, which does not change to brown, but soon disappears. The blue colour is also produced on placing zinc in a solution of chloride of tantalum in hydrochloric acid, to which a small quantity of water has been added; too much water, however, prevents its formation.

Before the blowpipe, tantalic acid dissolves abundantly in *phosphorus-salt*, forming a clear, colourless glass, which undergoes no alteration when heated in the inner flame, and does not turn red on addition of protosulphate of iron. With *borax* also it forms a transparent glass, which, however, if the quantity of tantalic acid is somewhat large, may be rendered opaque by interrupted blowing, or *flaming*, as it is technically called, but recovers its transparency by long exposure to a continued blast. A very large quantity of tantalic acid renders the glass opaque. No alteration takes place in the inner flame. With *carbonate of soda* on charcoal, tantalic acid produces effervescence, but does not fuse into a bead or undergo reduction.

The above-described characters are sufficient to distinguish tantalic acid from all the substances previously described. From titanic acid, which it most resembles, it is distinguished, first, by its behaviour before the blowpipe; secondly, by its perfect insolubility in strong sulphuric acid after ignition, ignited titanic acid, when finely pulverised, being soluble in that acid; and, thirdly, by the fact that, when it is fused with bisulphate of potash, and the fused mass treated with cold water, the tantalic acid remains undissolved in combination with sulphuric acid; whereas titanic acid, similarly treated, yields a fused mass, which dissolves completely in a considerable quantity of cold water, provided the fusion has been continued long enough. From silica, tantalic acid is distinguished by its behaviour before the blowpipe, silica being insoluble in phosphorus-salt, and fusing to a transparent bead when heated on charcoal with a small quantity of carbonate of soda. The behaviour of tantalic acid with zinc, with tincture of galls, and with hydrofluoric acid, also distinguishes it from silica.

Sulphide of tantalum, Ta_2S_3.—Obtained by igniting tantalic acid in the vapour of bisulphide of carbon, or by exposing chloride of tantalum to the action of hydrosulphuric acid gas. The product is not perfectly definite in either case. The second process yields a sulphide containing 24·08 per cent. sulphur, whereas the formula Ta_2S_3 requires 25·86 per cent. The former process gives a product containing 28·5 per cent. sulphur. Sulphide of tantalum is a black substance, which acquires a brass-yellow colour by trituration in an agate mortar. Heated in an atmosphere of chlorine gas, it is converted into chloride of tantalum and chloride of sulphur (H. Rose).

Chloride of tantalum, $TaCl_2$.—Prepared by passing chlorine gas over a heated mixture of tantalic acid and charcoal. Tantalic acid is mixed with starch or sugar, and the mixture completely charred by ignition in a covered crucible. It is then introduced in small pieces into a glass tube which is strongly heated by a charcoal fire, while a stream of dry carbonic acid is passed through it. As soon as all the moisture is expelled, the tube is left to cool, the flow of carbonic acid being still kept up; the carbonic acid apparatus is then replaced by a chlorine apparatus, and the tube again heated after the carbonic acid and atmospheric air have been completely expelled by the chlorine. Chloride of tantalum is then obtained in the form of a sublimate of a pure yellow colour. If, however, the tantalic acid contains tungstic acid, the colour of the sublimate is red; and if stannic or titanic acid is present, yellow drops of liquid chloride are also produced. Chloride of tantalum melts at 430°, and volatilises at 291°. Water decomposes it, forming hydrochloric and tantalic acids; but the decomposition is not complete even at the boiling heat: water containing a small quantity of ammonia decomposes the chloride perfectly even at ordinary temperatures. According to the recent experiments of H. Rose, chloride of tantalum contains 81·14 per cent. of tantalum.

Bromide of tantalum is prepared in the same manner as the chloride; when freed from excess of bromine, it has a yellowish colour.

Fluoride of tantalum, TaF_2.—Ignited tantalic acid does not dissolve in aqueous hydrofluoric acid; but the hydrate dissolves, forming a clear solution, which, when evaporated, partly gives off the tantalum as fluoride, but also leaves a white residue of oxyfluoride. Fluoride of tantalum forms with fluoride of potassium a crystalline double salt, containing $KF.2TaF_2$; and with fluoride of sodium the salt, $NaF.TaF_2$ (H. Rose).

ESTIMATION AND SEPARATION OF TANTALUM.

Tantalum is estimated in the form of anhydrous tantalic acid, containing 81·13 per cent. of the metal. It occurs in nature associated with lime, magnesia, yttria, and the oxides of iron and manganese, and occasionally with zirconia, titanic acid, and a few other substances. From these it is separated by fusion with hydrate of potash, or, better, with bisulphate of potash, in the manner already described (p. 279). Some compounds of tantalic acid may be decomposed by sulphuric acid, the tantalic acid being separated in the insoluble state, and all the bases passing into the solution.

Tantalate of *zirconia* may be decomposed in this manner. On treating that compound with strong sulphuric acid, and digesting the cooled mass for some time with a large quantity of water, sulphate of zirconia dissolves, and tantalic acid remains behind in combination with sulphuric acid, from which it may be purified by repeated boiling with water.

From *titanic acid*, with which it sometimes occurs in nature, tantalic acid is separated by fusing the mineral with bisulphate of potash, and treating the fused mass with a large quantity of water. Titanic acid then dissolves, especially if the water is slightly acidulated with hydrochloric acid, while sulphate of tantalic acid remains undissolved. The titanic acid is precipitated from the solution by boiling: the separation is, however, not very complete. In some cases, the decomposition may be effected by sulphuric acid.

From the *alkalies*, tantalic acid may be completely separated by sulphuric acid, provided the compound is soluble in water. In the contrary case, it must first be fused with carbonate or hydrate of potash. If, however, the quantity of alkali is to be likewise estimated, the compound must be rendered soluble by fusion with sulphate of ammonia.*

SECTION IX.

COLUMBIUM.

Synonyme. Niobium; Cb.

This metal was discovered by Hatchett in 1801, in a black mineral (columbite), from Massachusetts, in North America; it was thence named *Columbium*. Wollaston, in 1809, examined it further, and pronounced it to be identical with the tantalum discovered by Ekeberg, in Swedish tantalite. This idea of the identity of the two metals remained current till 1846, when H. Rose†, by a more careful investigation of the matter, was led to conclude that the American columbite, and the tantalite from Bodenmais, in Bavaria, contained two acids bearing a very close resemblance to tantalic acid, but nevertheless, distinct from it and from each other. To the metals supposed to exist in these acids he assigned the names *Niobium* and *Pelopium*. But by a later investigation‡, he finds that these two acids really contain the same metal, associated with different quantities of oxygen; he therefore discards the name pelopium, and proposes to designate by *niobium* the metal contained in American columbite and Bavarian tantalite. As, however, this metal is clearly the one discovered fifty years ago by Hatchett, we cannot do better than retain for it the name originally proposed by its discoverer, viz., COLUMBIUM.*

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* H. Rose, Handb. d. Anal. Chem. 1851, ii. 326—335.

† Pogg. Ann. lxiii. 317; lxix. 115.

‡ Pogg. Ann. xc. 456; Ann. Ch. Pharm. lxxxviii. 245.

Columbium likewise occurs, associated with yttrium, uranium, iron, and small quantities of other metals, in a Siberian mineral called urano-tantalite, yttro-ilmenite, or samarskite; also in pyrochlore, eukolite or wöhlerite, euxenite, and in a variety of pitchblende from Satersdälen.

Metallic columbium is obtained by passing dry ammoniacal gas over the chloride. It is a black powder, which oxidises when heated in the air. Nitric acid and aqua-regia have no effect upon it; but a mixture of hydrofluoric and nitric acids attacks it at ordinary temperatures. It combines with oxygen in two proportions, forming *columbous* and *columbic* acids, formerly supposed by Rose to contain different metals, and called respectively niobic and pelopic acids. The composition of these acids has not yet been determined.

Columbous acid, or a mixture of that acid with columbic acid, is separated from the minerals containing it by processes similar to those already described for the preparation of tantalic acid (p. 279); and when the acid, or mixture of acids, thus obtained, is mixed with charcoal and heated in a stream of chlorine gas, with the precautions already detailed for the preparation of chloride of tantalum (p. 285), it is generally converted into two chlorides,—the one white, volatile, but not fusible; the other yellow, likewise volatile, and easily fusible: the latter contains the larger proportion of chlorine. It was the formation of these two chlorides which led Rose to conclude that certain varieties of tantalite contained two distinct metals, niobium and pelopium; he now finds, however, that the substance which he regarded as perfectly pure niobic acid, obtained by the action of water on the white chloride, may, by mixing it with a large excess of charcoal, and gently igniting the mixture in a stream of chlorine gas, with strict attention to all the precautions above alluded to, be completely converted into the yellow chloride,—the so-called chloride of pelopium. But if a smaller quantity of charcoal be used, or if the mixture be too strongly ignited during the action of the chlorine, especially at the commencement, the white and less volatile chloride (chloride of niobium), is obtained, as well as the yellow compound.

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* See a paper "On the Nomenclature of the Metals contained in Columbite and Tantalite," by Prof. Connell, Phil. Mag. [4].

Columbium appears, then, to be capable of uniting with chlorine in two proportions; and the chlorides thus formed yield, when treated with water, two acids of corresponding constitution, viz., *Columbous* and *Columbic acids*, the latter, which contains the larger proportion of oxygen, being formed from the yellow chloride.

Columbous acid (Rose's niobic acid) may, like tantalic acid, be obtained in the amorphous and the crystalline state, viz., by the rapid or gradual action of water on the chloride. Its specific gravity is lower than that of tantalic acid, and is subject to similar variations. Samples of the acid, prepared from various sources, exhibited, after ignition over a spirit-lamp to the point of incandescence, specific gravities ranging from 4·66 to 5·26; by stronger ignition, the density was diminished. The mean density of the amorphous acid was found to be greater than that of the crystalline in the ratio of 1 to 0·875. The acid is colourless both in the anhydrous and hydrated states, but when heated assumes a yellow colour, much deeper than that of heated tantalic acid. The hydrated acid becomes incandescent during its transition to the anhydrous state.

Columbous acid is decomposed by ignition in a stream of hydrosulphuric acid, and converted into sulphide of columbium. When ignited in ammoniacal gas, it turns black, and yields a large quantity of water.

Columbous acid, after ignition, is insoluble in all acids. The hydrated acid is but very sparingly soluble in hydrochloric acid; so that when an alkaline columbite is precipitated by excess of hydrochloric acid, the filtrate retains only a trace of columbous acid in solution. The hydrated acid dissolves, to a certain extent, in oxalic and in hydrofluoric acid.

The *alkaline columbites* are soluble in water, in solutions of potash and carbonate of potash, but dissolve with great difficulty in excess of soda and carbonate of soda, more sparingly even than tantalate of soda. Columbous acid is precipitated from its alkaline solutions by acids, especially by sulphuric acid, even at ordinary temperatures; whereas the precipitation of tantalic acid requires the aid of heat. Oxalic acid does not affect alkaline columbites; but *carbonic acid* gas precipitates an acid salt soluble in a large quantity of water; *acetic acid* and *sal-ammoniac* also form precipitates. A solution of an alkaline columbite, acidulated with sulphuric or hydrochloric acid, forms a red precipitate with *ferrocyanide of potassium,* bright yellow with the *ferricyanide,* and orange-red with *infusion of galls.* A piece of *zinc,* immersed in the acidulated solution, forms a beautiful blue precipitate, which after a while changes to brown.

Before the blowpipe, especially in the inner flame, columbous acid assumes a greenish yellow colour while hot, but becomes colourless on cooling. With *borax* it forms in the outer flame a colourless bead, which, if the acid is in sufficient quantity, becomes opaque by flaming. In the inner flame, the bead assumes a greyish blue colour, provided it contains a sufficient quantity of acid to produce opacity on cooling. In *phosphorus-salt,* the acid dissolves in large quantity, forming a colourless bead in the outer flame, and in the inner, a violet-coloured, or, if the bead be saturated with the acid, a beautiful blue bead, the colour disappearing in the outer flame. The addition of protosulphate of iron changes the colour to blood-red. These characters, together with the above-mentioned precipitates, sufficiently distinguish columbous from tantalic acid.

Columbic acid (Rose's pelopic acid) bears a very strong resemblance to tantalic acid, and is intermediate in its properties between that acid and columbic acid. Its specific gravity ranges from 5·5 to 6·7. It appears to be susceptible of three modifications; viz., amorphous, crystalline befcre ignition, and crystalline after ignition at the heat of a porcelain-furnace. It is insoluble in all acids after ignition. It is precipitated from its alkaline solutions by the same reagents as columbous acid. The precipitate formed by hydrochloric acid redissolves in excess, forming an opalescent solution from which the acid is completely precipitated by sulphuric acid at a boiling heat. The acidulated solutions yield a brownish-red precipitate with *ferrocyanide of potassium*, white with *ferricyanide*, and orange-yellow with *infusion of galls*. *Zinc* behaves with these solutions in the same manner as with solutions of tantalic acid. A fine blue colour is obtained by treating the yellow chloride of columbium with hydrochloric acid, diluting with water, and adding a piece of zinc.

With *borax* before the blowpipe, columbic acid behaves like tantalic acid. In *phosphorus-salt* it dissolves in large quantity, forming a colourless bead in the outer flame. In the inner flame, the bead assumes a light-brown colour, tinged with violet, the colour disappearing again after a while in the outer flame. The addition of protosulphate of iron changes the brown colour to crimson.

It is remarkable that columbic acid cannot be formed directly from columbous acid, even by the most powerful oxidising agents. It appears, however, to be deprived of a portion of its oxygen by certain reducing agents.

The methods of estimating columbium and separating it from other metals are the same as for tantalum. No method is known of separating columbium from tantalum; but these metals have not hitherto been found occurring together.

Ilmenium. (?) — According to the observations of R. Hermann*, it would appear that Siberian yttrotantalite or yttroilmenite contains a peculiar metal, ilmenium, which forms an acid, ilmenic acid, very closely resembling columbous acid, but nevertheless distinct from it; the chief points of difference being the lower specific gravity, viz., 4·1 to 4·2; the insolubility of the hydrate in hydrochloric acid; and the formation of a compound with sulphuric acid which is decomposed by a large quantity of water, leaving a residue of hydrated ilmenic acid. H. Rose †, however, is of opinion that the supposed ilmenic acid is merely columbous [niobic] acid, more or less impure. The question must, for the present, be regarded as undecided. Rose likewise regards yttroilmenite as identical with urano-tantalite or samarskite.

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* J. pr. Chem. xxxviii. 91, 119; xl. 475; lxv. 54.

† Pogg. Ann. lxxi. 157.

ORDER VIII.

METALS WHOSE OXIDES ARE REDUCED TO THE METALLIC STATE BY HEAT (NOBLE METALS).

SECTION I.

MERCURY.

Eq. 100 *or* 1250; Hg.

Mercury, or quicksilver, as it is named from its fluidity, has been known from all antiquity. It is found to a small extent in the metallic state, but its principal ore is the native sulphide *cinnabar*. The most valuable European mines of mercury are, those of Almaden in Spain, and of Idria in Illyria. At Almaden the cinnabar is found in veins, often nearly fifty feet thick, traversing micaceous schists of the older transition period: in Illyria it is disseminated in beds of grit, bituminous schist, or compact limestone of more recent date. The mode of extraction in both these localities, consists in simply roasting the ore in a distillatory apparatus, whereby the sulphur is burned and converted into sulphurous acid, while the mercury is set free in the form of vapour, and condenses in chambers or vessels provided for it.

The arrangement adopted in Illyria is represented in figures 12, 13, 14. A is a large furnace (figs. 12 and 14), on each side of which is a series of condensing chambers, CCCCCD. The space V, separated from the fire-place by the perforated arch *n n′*, is filled with the ore in large lumps; smaller pieces are introduced into the next compartment above the arch *pp′*; and on the uppermost arch, *r r′*, are laid a number of earthen capsules, containing the pulverised ore and the mercurial residues of preceding operations. The fire being lighted, and the

Fig. 12.

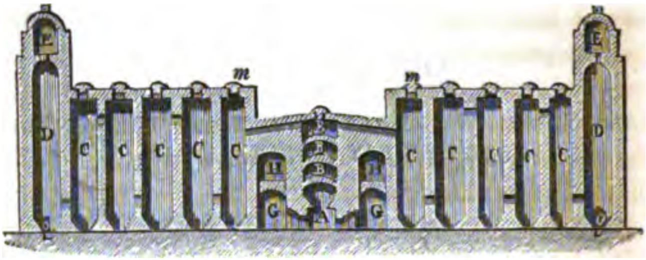


Fig. 13.

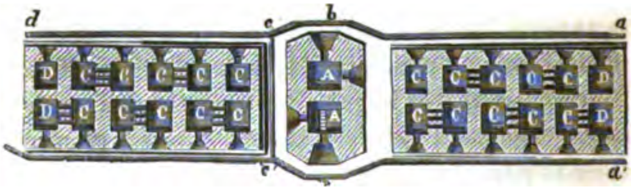
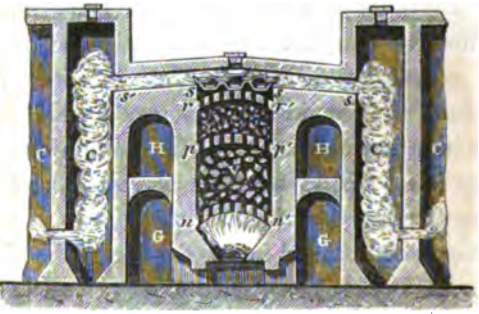


Fig. 14.



heat gradually raised, the sulphur is burned by the air which enters through channels opening into the spaces G, H; and the mixture of mercurial vapour, sulphurous acid, and smoke from the fire, passes through the horizontal channel at the top of the furnace, then up and down through the condensing chambers, C C C C, and finally escapes into the air.

The greater part of the mercury condenses in the first three chambers, whence it runs into the channels $abcd, a'b'c'd'$, which conduct it into a reservoir. To facilitate the condensation of the last portions of mercury in the chambers D D, the vapours are made to pass between a series of boards placed from side to side of these chambers in an inclined position, and having a stream of water continually running over them. As the mercury which condenses in these last chambers is mixed with a considerable quantity of dust, it is collected in separate channels, then filtered, and the residues returned to the furnace as already described.

The mercury obtained by this process is purified by filtration through coarse linen cloth, and sent into the market in wrought-iron bottles, each containing about fifty pounds.

At Almaden, the mercury is also extracted from the cinnabar by roasting, the operation being conducted in furnaces called *buytrones*. (Figs. 15 and 16.)

Fig. 15.

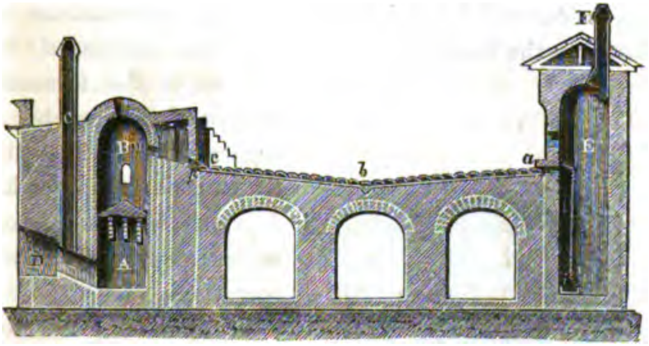
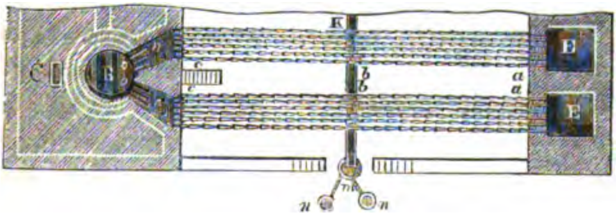


Fig. 16.



The fire is made at A, and the space B, above it, is filled with the ore, the largest pieces being laid on the perforated arch at the bottom, smaller pieces above, and the whole covered with lumps of a mixture of clay, powdered ore, and the residues of preceding operations. The vapours pass through an aperture *p*, in the upper part of the furnace, into a series of tubular vessels called *aludels*, open at both ends and fitting one into the other. These are laid on a surface *c, b, a*, called the *aludel-bath*, first descending a little, then ascending, and finally opening into the chimney. The form and disposition of the aludels is shown in figure 17. The condensed mercury escapes at the joints of the aludels, and runs into the channel *b b*, by which it is conveyed into the reservoirs *m, n n*. The uncondensed mercurial vapour passes into the chamber E, where it deposits a mercurial dust, which yields by filtration an additional quantity of liquid mercury, and a residue which is mixed with clay and pounded ore, and returned to the furnace in the manner above mentioned. The heating of the furnace is continued for twelve or thirteen hours: it is then left to cool for three or four days, after which it is cleared out and arranged for another operation.

Fig. 17.

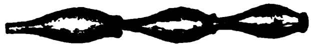
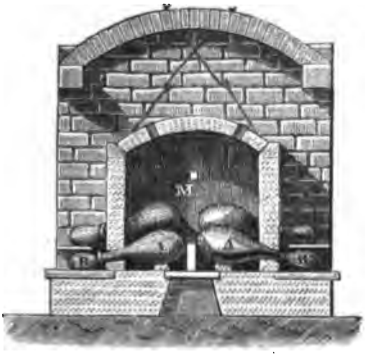


Fig. 18.



In the duchy of Deux Ponts, a mixture of cinnabar and limestone is heated to redness in retorts of earthenware or cast-iron placed side by side in an oblong furnace (fig. 18), and provided with receivers containing a certain quantity of water. Sulphide of calcium and sulphate of lime are then formed, and the mercury is evolved in vapour, which condenses in the receivers.

At Horzowitz, in Bohemia, a mixture of cinnabar and smithy-scales is placed in iron dishes, which are attached one above the other by the centres of their bases to a vertical iron axis, and covered with an iron receiver, closed at top and dipping into water at the bottom. The upper part of the receiver is surrounded by the furnace, and imparts its heat to the dishes, from which the mercury rises in vapour and collects in the water below.

The mercury of commerce is generally very pure; it is sometimes, however, contaminated with foreign metals, and in that case its fluidity is remarkably impaired.

Mercury may be purified by distilling it from half its weight of iron-turnings, or by digesting it with a small quantity of nitric acid, or with a solution of corrosive sublimate, which rids it of metals more oxidable than itself. The purification may also be effected by agitating the mercury with a small quantity of solution of sesquichloride of iron. Pure mercury should leave no residue when dissolved in nitric acid, evaporated, and ignited; when made to run down a slightly inclined surface, it should retain its round form, and not *drag a tail;* and when agitated in a bottle with dry air, it should not yield any black powder.

Mercury is liquid at ordinary temperatures. Its colour is white, with a shade of blue when compared with that of silver, and it has a high metallic lustre. At 39° or 40° below zero, it becomes solid, and crystallises in regular octohedrons. According to M. Kupffer, the density of mercury at 39·2° is 13·5886; at 62·6°, 13·5569; and at 78·8°, 13·535 (according to Kopp, it is 13·595 at 39·2°). In the solid state, its density is about 14·0. Mercury boils at 662°, forming a colourless vapour, the density of which was observed, by Dumas, to be 6976; the theoretical density is 6930. Mercury emits a sensible vapour between 68° and 80°, but not under 20° (Faraday). When heated near its boiling point, mercury absorbs oxygen from the air, and forms crystalline scales of the red oxide. It is not affected by boiling hydrochloric or dilute sulphuric acid, but is readily dissolved by dilute nitric acid. This metal never dissolves in hydrated acids by substitution for hydrogen. Mercury combines with oxygen in two proportions, forming the black oxide, Hg_2O, and the red oxide, composed of single equivalents, HgO, both of which are bases. According to these formulæ, the equivalent of mercury is assumed to be 100; but whether it should be this number or a multiple of it by 2, no certain means exist of deciding, while we are in ignorance of any isomorphous relation of mercury with the magnesian metals.

MERCUROUS COMPOUNDS.

Dioxide of mercury (*black oxide*), *Mercurous oxide,* Hg_2O, 208 or 2600. — This oxide is obtained by the action of a cold solution of potash, used in excess, upon calomel. The substances should be mixed briskly together in a mortar, in order that the decomposition may be as rapid as possible, and the oxide be left to dry spontaneously in a dark place. Mr. Donovan finds these precautions necessary, from the disposition of this oxide to resolve itself into metallic mercury and the higher oxide. The decomposition of mercurous oxide is promoted by elevation of temperature, and by exposure to light.

Mercurous oxide is a black powder, whose density is 10·69 (J. Herapath); it unites with acids and forms salts. Its soluble salts are all partially decomposed by pure water, which combines with a portion of their acid, and throws down a subsalt containing an excess of oxide. They are precipitated black by *hydrosulphuric acid* and *alkaline sulphides*. *Caustic alka-*

lies throw down a black precipitate of mercurous oxide. The *alkaline carbonates* precipitate white mercurous carbonate, which soon turns black from decomposition. *Carbonate of baryta* also decomposes mercurous salts, forming a mercuric salt which remains in solution, and a precipitate of metallic mercury. Mercurous salts are decomposed by *hydrochloric acid* and soluble *chlorides*, with precipitation of calomel as a white powder, a property by which they are distinguished from the salts of the red oxide of mercury. In very dilute solutions, only an opalescence is produced. The precipitate turns black when treated with potash or ammonia. Mercurous salts form with *phosphate of soda* a white precipitate of mercurous phosphate, and with *alkaline chromates*, a brick-red precipitate of mercurous chromate. *Oxalic acid* and *alkaline oxalates* form a white precipitate of mercurous oxalate. *Ferrocyanide of potassium* produces a thick white precipitate, and *ferricyanide of potassium* a red-brown precipitate. *Tincture of galls* yields a brownish-yellow precipitate.

The salts of this, and also of the red oxide, are reduced to the metallic state by copper and the more oxidable metals, and by the proto-compounds of tin; also by phosphorous and sulphurous acids. The precipitated mercury often takes the form of a grey powder, in which no metallic globules are perceptible, and remains in this condition while moist. Mercury in this divided state possesses the medicinal qualities of the milder mercurials, and has often been mistaken for black oxide. To obtain *precipitated mercury*, equal weights of crystallised protochloride of tin (salt of tin) and corrosive sublimate may be dissolved, the first in dilute hydrochloric acid and the second in hot water, and the solutions mixed, with stirring. The salt of tin takes up all the chlorine of the corrosive sublimate, becoming bichloride of tin, which remains in solution, while the mercury is liberated, and forms so fine a precipitate, that it requires several hours to subside. It may be washed by affusion of hot water and subsidence, and slightly drained on a filter, but not allowed to dry. There can be no doubt that it is in this divided state, and not as the black oxide, that mercury is obtained by trituration with fat, turpentine, syrup, saliva, &c., in many pharmaceutical preparations.

Disulphide of mercury, Hg_2S, is obtained, as a black precipitate, by the action of hydrosulphuric acid on a solution of mercurous nitrate or upon calomel. This sulphide is decomposed by a gentle heat, and resolved into globules of mercury and the higher sulphide.

Dichloride of mercury, Mercurous chloride, Calomel, Hg_2Cl, 235·5 or 2943·75. — A variety of processes are given for the preparation of this remarkable substance. It may be obtained in the humid way, by digesting 1⅛ parts of mercury with 1 part of pure nitric acid, of density from 1·2 to 1·25, till the metal ceases to dissolve, and the liquid has begun to assume a yellow tint. A solution is also prepared of 1 part of chloride of sodium in 32 parts of distilled water, to which a certain quantity of hydrochloric acid is added; and this, when heated to near the boiling point, is mixed with the mercurial salt. The mercury takes up the chlorine of the common salt, and the subchloride of mercury formed precipitates as a white powder, while the nitric acid and oxygen are given up by the mercury to the sodium, which becomes nitrate of soda:

$$NaCl + Hg_2O \, . \, NO_5 = Hg_2Cl + NaO \, . \, NO_5.$$

The excess of acid in this process is intended to prevent the precipitation of any subnitrate of mercury, which the dilution of the nitrate of mercury, on mixing the solutions, might occasion. Calomel is also obtained by rubbing together, in a mortar, 4 parts of protochloride of mercury (corrosive sublimate) with 3 parts of running mercury. The mixture is afterwards introduced into a glass balloon, and sublimed by a heat gradually increased. Here the protochloride of mercury combines with mercury, and the dichloride is produced. The same result is obtained by mixing mercuric sulphate with as much mercury as it already contains, and about one-third of its weight of chloride of sodium, and subliming the mixture. The vapour of the dichloride of mercury, in these sublimations, is advantageously condensed by conducting it into a vessel containing hot water; the vapour of the water then condenses the salt in an extremely fine and beautifully white powder. The product of this operation is recommended by its purity, as well as by its minute division; for the water dissolves out all the protochloride of mercury by which the dichloride is accompanied. It appears that whenever the dichloride is sublimed, a small portion of it is resolved into mercury and the protochloride. As the calomel usually condenses in a solid cake, it must, to prepare it for medical use, be reduced to a fine powder, and washed with hot water to remove the soluble chloride.

Dichloride of mercury is obtained by sublimation, in four-sided prisms, terminated by summits of four faces. When the solid cake is finely pounded, the salt acquires a yellow tinge. The density of this salt in the solid condition is 6·5; in the state of vapour 8350. One volume of the vapour contains one volume of vapour of mercury and half a volume of chlorine. This salt is so very sparingly soluble in water, that when mercurous nitrate is added to hydrochloric acid diluted even with 250,000 times its weight of water, a sensible precipitate of dichloride of mercury appears. When boiled for a long time in hydrochloric acid, this salt is resolved into protochloride of mercury which dissolves, and mercury which is reduced.

Action of ammonia on dichloride of mercury.—The dry dichloride was found by Rose to absorb an equivalent of ammonia, and to become black. Exposed to air, the compound loses its ammonia, and the dichloride of mercury recovers its white colour. This ammoniacal compound is

$Hg_2Cl.NH_3$, and may be regarded as $\left.\begin{matrix}\overbrace{NH_3Hg}\\ Hg\end{matrix}\right\}Cl$, that is, as dichloride of mercury in which 1 eq. of mercury is replaced by mercurammonium, $\overbrace{NH_3Hg}$. Or again, if we suppose the mercurous salts to contain, not two distinct atoms, but a *double atom* of mercury ($Hg' = Hg_2$), this double atom being the equivalent of one atom of hydrogen — thus, calomel $= Hg'Cl$; black oxide of mercury $= Hg'O$, &c.,— then the ammoniacal compound $Hg_2Cl.NH_3$ may be regarded as *chloride of mercurosammonium*, $\overbrace{NH_3Hg'}.Cl$, or chloride of ammonium in which one eq. H is replaced by a double atom of mercury.

When calomel is digested in aqueous ammonia, it turns black, and was found by Kane to be converted into *mercurous amido-chloride*, $Hg_2Cl.Hg_2NH_2$, sal-ammoniac being formed at the same time:

$$2Hg_2Cl + 2NH_3 = Hg_2Cl.Hg_2NH_2 + NH_4Cl.$$

This compound may also be regarded as *chloride of bimercurosammonium*, $\overbrace{NH_2Hg'_2}.Cl$. It is not altered by boiling water; when quite dry, it is of a grey colour.

Dibromide of mercury, Mercurous bromide, Hg_2Br, is a white insoluble powder, resembling in all respects the dichloride, and formed in similar circumstances. A boiling solution of bromide of strontium was found by Lœwig to dissolve three equivalents of dibromide of mercury, of which one equivalent precipitated during the cooling of the solution. When the filtered solution was evaporated, it deposited a salt in small crystals, containing $SrBr.2Hg_2Br$. These crystals were decomposed by pure water, and resolved into the insoluble dibromide, Hg_2Br, and a double salt, $SrBr.Hg_2Br$, which dissolved easily, and crystallised by evaporation.

Diniodide of mercury, Mercurous iodide, Hg_2I, is obtained by precipitation as a green powder, which is red when heated. It is also formed by triturating mercury and iodine together in a mortar, with a few drops of alcohol, in the proportion of 2 eq. of the former to 1 eq. of the latter.

No *dicyanide of mercury* exists; and it is doubtful whether a *difluoride*, corresponding with the dioxide, has been formed.

Mercurous carbonate, Carbonate of black oxide of mercury, $HgO_2.CO_2$, precipitates as a white powder, when an alkaline carbonate is added to the nitrate of the same oxide. The precipitate becomes grey when the liquid containing it is boiled, and carbonic acid escapes. This carbonate is soluble both in carbonic acid water, and, to a slight extent, in an excess of alkaline carbonate.

Mercurous sulphate, Sulphate of black oxide of mercury, $Hg_2O.SO_3$; 248 *or* 3100.—This salt is obtained by digesting 1 part of mercury in 1½ parts of sulphuric acid, avoiding a high temperature, and interrupting the process as soon as all the mercury is converted into a white salt. It is also precipitated when sulphuric acid is added to a solution of mercurous nitrate. The salt may be washed with a little cold water. It crystallises in prisms, and requires 500 times its weight of cold and 300 of hot water to dissolve it. With aqueous ammonia this salt forms a dark grey powder, containing ammonia or its elements.

Mercurous seleniate.—Aqueous solutions of seleniate of soda and mercurous nitrate form a white precipitate, probably consisting of the neutral salt, $Hg_2O.SeO_3$, which, however, gradually turns yellow during washing, and, when dried at 100°, is found to be reduced to $6Hg_2O.5SeO_3$ (Körner).

Mercurous selenite.—The neutral salt $Hg_2O.SeO_2$ is found native as *onofrite*, a yellow earthy mineral, occurring, together with horn-quicksilver and native mercury, at San Onofrio, in Mexico. It is also obtained by double decomposition as a white powder, which melts at 356°, and when heated above that point, is converted into a brick-red, opaque, crystalline mass of the salt $3Hg_2O.4SeO_2$ (Köhler).*

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* Pogg. Ann. lxxxix. 146.

Mercurous nitrates, Nitrates of black oxide of mercury.—The *neutral nitrate* is obtained when mercury is dissolved in an excess of cold nitric acid: it crystallises readily in transparent rhombs. It is soluble with heat in a small quantity of water, but is decomposed by a large quantity of water, and an insoluble subsalt formed, unless nitric acid be added to the water. The formula of this salt is $Hg_2O.NO_5 + 2HO$. A *subnitrate* is formed when the black oxide is dissolved in a solution of the preceding salt, or when an excess of mercury is digested in diluted nitric acid at the usual temperature. It crystallises readily in white, opaque rhombic prisms, which contain, according to both G. Mitscherlich and Kane, $3Hg_2O.2NO_5 + 3HO$; or, according to Marignac, $4Hg_2O.3NO_3 + HO$. This salt was observed by G. Mitscherlich to be dimorphous. When dissolved by dilute nitric acid, it yields the neutral salt. The subnitrate is soluble in a little water, but when treated with a large quantity, it leaves undissolved, like the neutral nitrate, a white powder, which retains its colour so long as the supernatant liquid is acid, but becomes yellow when washed with water. The *yellow subnitrate of mercury* was found to contain $2Hg_2O.NO_5 + HO$ (Kane). Another subnitrate, containing, according to Marignac, $5Hg_2O.3NO_5 + 2HO$, is obtained by boiling the solution or the mother-liquor of the neutral or the sesquibasic nitrate with excess of mercury for several hours. This salt crystallises in colourless or slightly yellow crystals, derived from an unsymmetrical oblique prism; it appears to be the most stable of all the mercurous subnitrates. When very dilute ammonia is added to the preceding soluble nitrates, without neutralising the whole acid, a velvety black precipitate falls, known as *Hahnemann's soluble mercury*. This salt contains, according to the analysis of C. G. Mitscherlich, $3Hg_2O.NO_5 + NH_3$. But when pains were taken to avoid decomposition of the salt in washing it, its composition was found by Kane to be $2Hg_2O.NO_5 + NH_3$. Bibasic mercurous nitrate, mixed in solution with nitrate of lead, yields a crystalline double salt, containing $2(PbO.NO_5) + 2Hg_2O.NO_5$; and similar double salts with the nitrates of baryta and strontia (G. Staedeler).

Mercurous acetate, $Hg_2O . C_4H_3O_3$, falls when acetic acid, or an acetate, is added to the nitrate, in crystalline scales of a pearly lustre. It is anhydrous, and sparingly soluble in water.

MERCURIC COMPOUNDS.

Protoxide of mercury (*red oxide*), *Mercuric oxide*, HgO, 108 *or* 1351.—This compound is formed, as described, by the oxidation of mercury at a high temperature, or by heating the nitrate of mercury till all the nitric acid is expelled, and the mass, calcined almost to redness, no longer emits vapours of nitric oxide. As prepared by the latter process, protoxide of mercury forms a brilliant orange-red powder, crystallised in plates, and having the density 11·074. It is very dark red at a high temperature, but becomes paler as it cools. When reduced to a fine powder, it becomes yellow, like litharge, without any shade of red. It was found by Mr. Donovan to be soluble to a small extent in water, forming a solution which has a slight alkaline reaction. If contaminated with nitric acid, it gives off nitrous fumes when heated in a glass tube, and forms a yellow sublimate of subnitrate. This oxide is known in pharmacy as *red precipitate*. The same compound is obtained by precipitation, when a solution of corrosive sublimate is mixed with an excess of caustic potash; it then forms a dense powder of a lemon-yellow colour. It is necessary to use the potash in excess, otherwise a dark brown oxychloride is formed. The precipitated oxide parts with a little moisture when gently heated, but does not change in appearance. This yellow precipitated oxide differs in some respects from the red oxide; it combines in the cold with oxalic acid, whereas the red oxide does not; it is converted into black oxychloride by the action of an alcoholic solution of mercuric chloride, which has no action on the red oxide, and it is attacked by chlorine much more readily than the latter. At a red heat, the oxide of mercury is entirely volatilised in the form of oxygen and metallic mercury; the same decomposition takes place more slowly under the influence of light. The oxide detonates when heated with sulphur, and converts chlorine into hypochlorous acid.

The salts of mercuric oxide, when they do not contain a coloured acid, are colourless in the neutral, and yellow in the basic state. They have a disagreeable metallic taste, and act as violent acrid poisons. Some of them, *e.g.* the nitrate and sulphate, are resolved by water into a soluble acid salt, and an insoluble basic salt. From their aqueous solutions the mercury is, for the most part, precipitated in the metallic state by the same substances as from mercurous salts; but the complete reduction of the mercury is often preceded by the formation of a mercurous salt: such, for example, is the action of phosphorous acid, sulphurous acid, protochloride of tin, metallic copper, &c. *Gold* does not by itself reduce mercury from its salts; but if a drop of a mercuric solution be laid on a piece of gold, and a bar of zinc, tin, or iron be brought in contact with the moistened surface, an electrolytic action is set up, and the gold becomes amalgamated at the point of contact. *Hydrosulphuric acid* and *alkaline sulphides*, added in excess to mercuric salts, throw down a black precipitate of mercuric sulphide, insoluble in strong nitric acid. If, however, the quantity of the re-agent added is not sufficient for complete decomposition, a white precipitate is formed consisting of a compound of mercuric sulphide with the original salt, and often coloured yellow or brown by excess of the sulphide: this re-action is quite peculiar to mercuric salts. *Ammonia* and *carbonate of ammonia* form white precipitates, generally consisting of a compound of the mercuric salt with amide of mercury. The *fixed alkalies* throw down a yellow precipitate of mercuric oxide (not hydrated), insoluble in excess. If, however, the solution contains a large quantity of free acid, no red precipitate is formed, or only a slight one after a considerable time. *Monocarbonate of potash* or *soda* throws down red-brown mercuric carbonate. But if any ammoniacal salt is present in the solution, the fixed alkalies and their carbonates throw down the white precipitate above mentioned. *Bicarbonate of potash* or *soda* also gives a brown-red precipitate, with mercuric nitrate or sulphate; but with the chloride it forms a white precipitate which afterwards turns red. The *carbonates of baryta, strontia,* and *lime* precipitate mercuric oxide from the solutions of the sulphate and nitrate, but not from the chloride. *Phosphate of soda* throws down white mercuric phosphate from the sulphate and nitrate, but not from the chloride. *Chromate of potash* forms a yellowish red precipitate. *Ferrocyanide of potassium* forms, in solutions not too dilute, a white precipitate which gradually turns blue. *Tincture of galls* forms an orange-yellow precipitate with all mercuric solutions except the chloride. *Iodide of potassium* produces a scarlet precipitate of mercuric iodide, soluble in excess either of the mercuric salt or of iodide of potassium.

When aqueous ammonia is digested for several days upon precipitated oxide of mercury, the latter is converted into a yellowish white powder, which Kane regards as $2HgO . HgNH_2 + 3HO$, or as a hydrated compound of amide and oxide of mercury, which may be called oxyamide of mercury. According to Millon*, on the other hand, its composition is $4HgO . NH_3 + 2HO$, or rather $3HgO . HgNH_2 . HO + 2HO$. This substance, when placed in vacuo over quick lime, gives off 2 eq. water, turns brown, and in that state undergoes no further alteration by exposure to the air at ordinary temperatures; but between 100° and 130° C., it gives off a third atom of water and is reduced to the anhydrous compound $3HgO . HgNH_2$. The yellow hydrated compound rapidly absorbs carbonic acid from the air, and turns white. Dilute potash has no action upon it; but very strong potash, at a boiling heat, decomposes it, with evolution of ammonia. The brown anhydrous compound resists the action of aqueous potash even at the boiling heat, but is decomposed by fusion with hydrate of potash. Oxyamide of mercury is a powerful base, and expels ammonia from its salts. One equivalent of this compound, represented by the formula $3HgO . HgNH_2$, saturates 1 eq. of sulphuric acid, nitric acid, &c.; thus the sulphate is $3HgO . HgNH_2 . SO_3$; the nitrate, $3HgO.HgNH_2 . NO_5 + HO$, &c. &c.

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* Compt. rend. xxi. 826.

Nitride of mercury, Mercurammonia, NHg_3. — This compound is formed by passing dry ammoniacal gas over precipitated mercuric oxide previously well washed and dried:

$$3HgO + NH_3 = NHg_3 + 3HO.$$

After removing the excess of mercuric oxide by dilute nitric acid, the mercurammonia is obtained in the form of a dark flea-brown powder, which explodes, by heat, friction, percussion, or by contact with oil of vitriol, almost as violently as iodide of nitrogen. When carefully heated with hydrate of potash, it is decomposed without detonation, yielding ammoniacal gas and sublimed metallic mercury. It is also decomposed by hydrochloric acid, sulphuric, and concentrated nitric acid, yielding an ammoniacal and a mercuric salt. It may be regarded as ammonia in which the hydrogen is entirely replaced by an equivalent quantity of mercury (Plantamour).*

By the action of various ammoniacal salts at a boiling heat on mercuric oxide, compounds are obtained consisting of nitride of mercury combined with mercuric salts: *e.g.* with

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* Ann. Ch. Pharm. xl. 115.

nitrate of ammonia, the compound $NHg_3 + 2(3HgO.NO_5)$ is obtained; with *phosphate* of ammonia, the compound $NHg_3 + 3HgO.PO_5 + 2HO$; with *carbonate* of ammonia, the compound $2(NHg_3 + HgO.CO_2 + 2HO) + HO$; with *chromate* of ammonia, the compound $NHg_3.HgO.2HO + 4(HgO.CrO_3)$, which when treated with ammonia is converted into $NHg_3 + HgO.CrO_3 + 2HO$; with *acetate* of ammonia, the compound $NHg_3 + C_4H_3HgO_4 + 4HO$, &c. &c. (Hirzel).*

Protosulphide of mercury, Mercuric sulphide, Cinnabar, HgS; 116 *or* 1450.—This is the common ore of mercury, and sometimes occurs crystallised, forming a beautiful vermilion. It is prepared artificially by fusing one part of sulphur in a crucible, and adding to it by degrees six or seven parts of mercury, stirring it after each addition, and covering it to preserve it from contact of air, when it inflames, from the heat evolved in the combination. The product is exposed to a sand-bath heat, to expel the sulphur uncombined with mercury, and afterwards sublimed in a glass matrass at a red heat. A brilliant red mass of a crystalline structure is thus obtained, which, when reduced to fine powder, forms the lively red pigment vermilion. This sulphide is black before sublimation. It is precipitated black also when hydrosulphuric acid is passed through a solution of corrosive sublimate, but is of the same composition in both states. The sulphide of mercury, however, may be obtained of a red colour without sublimation, or in the humid way, by several methods.

Liebig recommends for this purpose to moisten the preparation called white precipitate, recently prepared, with sulphide of ammonium, and allow them to digest together. The black sulphide is instantly produced, which in a few minutes passes into a fine red cinnabar, the colour of which is improved by digesting it at a gentle heat in a strong solution of hydrate of potash. The sulphide of ammonium used in this experiment is prepared by dissolving sulphur to saturation in hydrosulphate of ammonia. Cinnabar is not attacked by sulphuric, nitric or hydrochloric acid, or by solutions of the alkalies, but is dissolved by aqua-regia.

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* Ann. Ch. Pharm. lxxxiv. 258.

Protochloride of mercury, Mercuric chloride, Corrosive sublimate, 135·5 *or* 1693·75. — This compound may be formed by dissolving red oxide of mercury in hydrochloric acid, or by adding hydrochloric acid to any soluble salt of that oxide; but it is generally prepared in a different manner. Four parts of mercury are added to five parts of sulphuric acid, and the mixture boiled till it is converted into a dry saline mass. The mercuric sulphate thus obtained is mixed with an equal weight of common salt, and heated strongly in a retort by a sand-bath; chloride of mercury sublimes and condenses in the upper part and neck of the retort, while sulphate of soda remains behind with the excess of chloride of sodium. The mercury and sodium have exchanged places in the salts:

$$NaCl + HgO . SO_3 = HgCl + NaO . SO_3.$$

Mercury, when heated in a stream of chlorine gas, burns with a pale flame, and is converted into a white sublimate of chloride. The salt has been prepared on a large scale in this manner, which was suggested as a manufacturing process by Dr. A. T. Thomson.

The sublimed chloride of mercury forms a crystalline mass, the density of which is 6·5; it fuses at 509°, and boils at about 563°. The vapour of chloride of mercury is colourless, its density 9420, one volume of it containing 1 volume of mercury vapour and 1 volume of chlorine gas. This salt is soluble in 16 parts of cold and in 3 parts of boiling water, in $2\frac{1}{3}$ parts of cold and in $1\frac{1}{6}$ part of boiling alcohol, and in 3 parts of cold ether. It is not decomposed by sulphuric or nitric acid; is largely dissolved by the latter, and also by hydrochloric acid. It is obtained by sublimation and from solution in two different crystalline forms. The solutions of chloride of mercury exposed to the direct rays of the sun evolve oxygen, while hydrochloric acid is dissolved and dichloride of mercury precipitates. The decomposition of this salt by the action of light is much more rapid when the solution contains organic matter. The poisonous action of chloride of mercury, which is scarcely inferior to that of arsenious acid, is best counteracted by liquid albumen, with which chloride of mercury forms an insoluble and inert compound.

Many metals, viz. arsenic, antimony, bismuth, zinc, tin, lead, iron, nickel, and copper, decompose mercuric chloride in the dry way, withdrawing the half or the whole of its chlorine, and separating calomel or metallic mercury, which latter forms an amalgam with the excess of the other metal. Arsenic forms terchloride of arsenic and a brown sublimate. An intimate mixture of 3 pts. antimony and 1 pt. corrosive sublimate, well pressed into a glass, becomes hot and liquid in the course of half an hour, and on the application of heat yields terchloride of antimony and metallic mercury. Tin heated with corrosive sublimate yields a distillate of bichloride of tin, and a grey residue containing calomel and protochloride of tin. Many metals also reduce the mercury from the aqueous or alcoholic solution of the chloride (p. 306). Most metals throw down calomel together with the mercury; but zinc, cadmium, and iron precipitate nothing but mercury, zinc being thereby converted into a semi-fluid amalgam, and cadmium forming an amalgam which crystallises in beautiful needles. The other reactions of mercuric chloride in solution have been already described (p. 306, 307.).

Chloride of mercury with ammonia.—1. When chloride of mercury is gently heated in a stream of ammoniacal gas, the latter is absorbed, and the compound fuses from heat evolved in the combination. The product was found by Rose to contain $2HgCl . NH_3$. This compound boils at 590°, and may be distilled without loss of ammonia; it is decomposed by water. — 2. *Fusible white precipitate.* When the double chloride of mercury and ammonium, called sal alembroth, is precipitated by potash in the cold, a white powder is obtained, which was first distinguished by Wöhler from the compound next described; its composition may be expressed, according to Kane's analysis, by the formula $HgCl \cdot NH_3$. The same compound is also formed when ammonia is added to a solution of sal-ammoniac, the liquid brought to the boiling point, and chloride of mercury dropt into it so long as the precipitate which is produced is redissolved. The compound appears, on the cooling of the solution, in small crystals, which are garnet dodecahedrons (Mitscherlich). The crystalline form of this compound belongs, therefore, to the regular system, like that of sal-ammoniac.

3. *Mercuric amido-chloride.*—The compound known as *white precipitate*, and sometimes *infusible white precipitate*, to distinguish it from the preceding, is formed when ammonia is added to a solution of chloride of mercury. When first produced, it is bulky and milk-white; it is decomposed by hot water or by much washing with cold water, and acquires a yellow tinge. Kane has shown that white precipitate is free from oxygen, and contains nothing but the elements of a double chloride and amide of mercury, and represents it by the formula $HgCl \cdot HgNH_2$. White precipitate is distinguished from calomel by solution of ammonia, which does not alter the former, but blackens the latter: it is readily dissolved by acids.

4. *Nitrochloride of mercury.*—Mitscherlich has observed that when white precipitate is gradually heated in a metal bath, and the heat continued for a long time, three atoms of it give off two atoms of ammonia and one atom of chloride of mercury, while a red matter remains in crystalline scales, having much the appearance of red oxide of mercury produced by the oxidation of the metal in air, and containing two atoms of chloride of mercury united with a compound of one atom of nitrogen and three atoms of mercury,

$2HgCl.NHg_3$. He concludes that the atom of white precipitate should be multiplied by three; its decomposition by the heat of the metal bath will then be represented by the equation:—

$$3(HgCl.HgNH^2) = 2HgCl.NHg_3 + 2NH_3 + HgCl.$$

The red compound is itself decomposed by a temperature above 680°, and resolved into chloride of mercury, mercury, and nitrogen. It is insoluble in water, and is not altered in boiling solutions of the alkalies. It may be boiled without change in diluted or concentrated nitric acid, and in pretty concentrated sulphuric acid, but it is decomposed and dissolved when boiled in the most concentrated sulphuric acid or in hydrochloric acid; no gas is evolved, but ammonia and chloride of mercury are found in the acid solution. The compound NHg_3 is not isolated by passing ammonia over the heated red compound. Mercury conducts itself in these compounds in the same way as potassium with ammonia, the olive-coloured substance produced by the action of dry ammonia upon potassium being the amide of potassium, $3(K.NH_2)$, and the plumbago-looking substance left on heating the amide of potassium, when ammonia escapes, a compound of nitrogen and potassium, NK_3.*

5. When white precipitate is boiled in water, it is changed into a heavy *canary-yellow powder*, which Kane regards as a compound of the amido-chloride of mercury with oxide of mercury, $HgCl.HgNH_2.2HgO$. Two atoms of water are decomposed in its formation, yielding the two atoms of oxygen which are found in the yellow compound, while the two atoms of hydrogen, added to an atom of chlorine and an atom of amidogen, form an atom of hydrochlorate of ammonia, which is found in solution:

$$2(HgCl.HgNH_2) + 2HO = HgCl.HgNH_2.2HgO + NH_4Cl.$$

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* Mitscherlich in Poggendorff's Annalen, vol. xxxix. p. 409.

Solutions of potash and soda convert white precipitate into the same yellow substance, while a metallic chloride is formed and ammonia evolved (Kane).

The five compounds just described may be regarded as salts of metalloïdal radicals formed from ammonium (NH_4) in which the whole or part of the hydrogen is replaced by an equivalent quantity of mercury. Thus, the fusible white precipitate, $HgCl.NH_3$, may be regarded as a *chloride of mercurammonium*, $= Cl.N\left\{\begin{matrix}H_3\\Hg\end{matrix}\right.$; the preceding compound, $2HgCl.NH_3$, as a double chloride consisting of the same compound united with chloride of mercury, namely as $ClHg + Cl.N\left\{\begin{matrix}H_3\\Hg\end{matrix}\right.$; similarly, infusible white precipitate, $HgCl.HgNH^2$, is a *chloride of bimercurammonium*, $ClN\left\{\begin{matrix}H_2\\Hg_2\end{matrix}\right.$; the yellow powder obtained by boiling this compound with water is a *chloride of tetramercurammonium* combined with two atoms of water, $= ClNHg_4 + 2HO$; and the red compound, $2HgCl.NHg_3$, may be regarded as a compound of this same chloride with chloride of mercury, namely as $ClHg.ClNHg_4$.

Oxychloride of mercury.—When a solution of corrosive sublimate is precipitated by potash or soda, mercuric oxide goes down, in combination with a portion of chloride, as a brown precipitate, unless a considerable excess of alkali be employed. The same oxychloride is produced by an alkaline carbonate; but a double carbonate is then also formed. Chloride of mercury is not immediately precipitated by the bicarbonates of potash and soda; and hence that salt may be employed to detect the presence of a neutral alkaline carbonate in these bicarbonates. This oxychloride may also be formed by passing chlorine through a mixture of water and oxide of mercury. It may be obtained crystalline and of a very dark colour, almost black, by mixing corrosive sublimate with chloride of lime, and boiling the liquid, or by treating a solution of corrosive sublimate with bicarbonate of potash, and allowing the solution to stand in an open vessel, when carbonic acid gradually escapes, and the compound $HgCl.4HgO$ is deposited. This oxychloride is decomposed by a moderate heat, chloride of mercury subliming, while the red oxide remains.

Sulphochloride of mercury, $HgCl.2HgS$. — When hydrosulphuric acid gas is passed through a solution of chloride of mercury, the precipitate which first appears, and does not subside readily, is white; it has been shown by Rose to be a compound of chloride and sulphide of mercury. This substance is changed entirely into sulphide of mercury, when left in water containing hydrosulphuric acid. On the other hand, precipitated sulphide of mercury digested in a solution of chloride of mercury, takes down that salt, and forms the compound in question. The same compound may be formed in the dry way, by fusing protosulphide of mercury (either black or red) with eight or ten times its weight of corrosive sublimate, in a sealed tube, and dissolving out the excess of chloride by boiling water; the sulphochloride then remains *in the form of a dirty-white powder* having a distinctly crystalline structure (R. Schneider). Sulphide of mercury combines likewise with the bromide, iodide, fluoride, and nitrate of mercury, and always in the proportion of two atoms of the sulphide to one atom of the other salt.

Double salts of chloride of mercury.—Chloride of mercury was found by M. Bonsdorff to combine with *chloride of potassium* in three different proportions, forming a series of salts in which the chloride of potassium remains as one equivalent, while the chloride of mercury goes on increasing. They are $KCl.HgCl.HO$, which crystallises in large transparent rhomboidal prisms; $KCl.2HgCl.2HO$ crystallising in fine needle-like amianths; and $KCl+4HgCl+4HO$, which crystallises also in fine needles. *Chloride of sodium* forms only one compound, $NaCl . 2HgCl . 4HO$, which crystallises in fine regular hexahedral prisms. One of the double salts of *chloride of ammonium* has long been known as *sal alembroth.* It crystallises in flattened rhomboidal prisms, $NH_4Cl . HgCl . HO$, and is isomorphous with the corresponding potassium salt. When exposed to dry air, it gives off its water without change of form. Kane has also obtained $NH_4Cl . 2HgCl$, and the same with an atom of water, $NH_4Cl . 2HgCl . HO$, the first in a rhomboidal form, and the second in long silky needles. All these double chlorides are obtained by dissolving their constituent salts together in the proper proportions. The *chlorides of barium* and *strontium* form well-crystallised compounds with *chloride of mercury,* viz. $BaCl . 2HgCl . 4HO$, and $SrCl . 2HgCl . 2HO$. *Chloride of calcium* combines in two proportions with mercuric chloride. When chloride of mercury is dissolved to saturation in chloride of calcium, tetrahedral crystals separate from the solution, which are tolerably persistent in air, and contain $CaCl . 5HgCl . 8HO$. After the deposition of these crystals, the liquid yields, when evaporated by a gentle heat, a second crop of large prismatic crystals, $CaCl . 2HgCl . 6HO$, which are very deliquescent. *Chloride of magnesium* also forms two salts, $MgCl.3HgCl.HO$, and $MgCl.HgCl.6HO$, both deliquescent. *Chloride of nickel* gives two compounds, one of which crystallises in tetrahedrons, like the chloride of calcium salt. *Chloride of manganese* forms a compound in good crystals, $MnCl . HgCl . 4HO$. The *chlorides of iron* and *zinc* form similar isomorphous salts, $FeCl . HgCl . HO$, and $ZnCl . HgCl . HO$. The double chlorides of zinc and of manganese are remarkable in one respect, that chloride of mercury dissolved by them in excess crystallises by evaporation in fine large crystals, such as cannot be obtained in any other way. The *chlorides of cobalt, nickel,* and *copper* form similar crystallisable salts; but chloride of lead does not appear to form a double salt with chloride of mercury. (Bonsdorff.)

Mercuric chloride likewise forms definite compounds with *alkaline chromates.* A hot solution of equal parts of mercuric chloride and *bichromate of ammonia* deposits, on cooling, large hexagonal prisms, of a splendid red colour, containing $NH_4O.2CrO_3 + HgCl + HO$, and the mother-liquor deposits a further crop of red, somewhat needle-shaped crystals, containing $3(NH_4O.2CrO_3) + HgCl$. (Richmond and Abel.*) *Monochromate of potash* forms with mercuric chloride a brick-red precipitate of mercuric chromate; and, on evaporating the filtered liquid, small pale red crystals are obtained of a double salt, containing $KO.CrO_3 + HgCl$. A solution of equivalent quantities of mercuric chloride and *bichromate of potash* yields beautiful red pointed crystals, containing $KO.2CrO_3 + HgCl$. (Darby.†) On mixing the cold saturated aqueous solutions of *acetate of copper* and mercuric chloride, and leaving the mixture to evaporate, deep blue, concentric, radiated hemispheres are obtained, containing $CuO.C_4H_3CuO_4 + HgCl$. (Wöhler and Hütteroth.)‡

Protobromide of mercury, Mercuric bromide, HgBr; 180 or 2250.—This salt is obtained by treating mercury with water and bromine. It is colourless, soluble in water and alcohol, and when heated, fuses and sublimes, exhibiting a great analogy to chloride of mercury in its properties. Its density in the state of vapour is 12370. Bromide of mercury forms a similar compound with sulphide of mercury $HgBr.2HgS$, which is yellowish. It was also combined, by Bonsdorff, with a variety of alkaline and earthy bromides. Bromide of mercury combines with half an equivalent of ammonia, in the dry way, and also gives, with solution of ammonia, a white precipitate, analogous to that derived from chloride of mercury.

Protiodide of mercury, mercuric iodide, HgI, 226·36 *or*

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* Chem. Soc. Qu. J. iii. 202.

† Chem. Soc. Qu. J. i. 24.

‡ Ann. Ch. Pharm. liii. 142.

2829·5.—Falls as a precipitate of a fine scarlet colour, when iodide of potassium is added to a solution of chloride of mercury. It may also be obtained by triturating its constituents together, in the proper proportion, with a few drops of alcohol. To procure it in crystals, Mitscherlich dissolves iodide of mercury to saturation, in a hot concentrated solution of the iodide of potassium and mercury, and allows the solution to cool gradually. When heated moderately, mercuric iodide becomes yellow; at a higher temperature, it fuses and sublimes, condensing in rhomboidal plates of a fine yellow colour. The forms of the red and yellow crystals are totally different, so that the change of colour is due to the dimorphism of mercuric iodide. The yellow crystals generally return gradually into the red state when cold; and this change may be determined at once by scratching the surface of a crystal, or by crushing it. The density of mercuric iodide in the state of vapour is 15630; it is the heaviest of gaseous bodies. Mercuric iodide is slightly soluble in water, but requires more than 6000 times its weight of water to dissolve it. It is much more soluble in alcohol and in acids, particularly with the assistance of heat. Mercuric iodide is very soluble in iodide of potassium; it is also dissolved by a solution of mercuric chloride, especially when hot. Hence, when a few drops of iodide of potassium solution are added to a solution of corrosive sublimate, a precipitate is formed, which redissolves on agitating the liquid; a somewhat larger quantity of iodide of potassium renders the precipitate permanent; and a still further addition causes it to disappear entirely.

When treated with sulphuretted hydrogen water, mercuric iodide forms the compound $HgI.2HgS$, which is yellow. Mercuric iodide unites with other iodides, and forms a class of salts as extensive as the compounds of chloride of mercury. They have been studied by M. P. Boullay.* Mercuric iodide also combines with chlorides; it is dissolved by a hot solution of mercuric chloride, and two compounds have been obtained on the cooling of the solution, viz., a yellow powder, $HgI.HgCl$, and white dendritic crystals, $HgI.2HgCl$.

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* Ann. Ch. Phys. [2], xxxiv. 337.

Mercuric iodide treated with very strong aqueous ammonia forms the compound $\overbrace{NH_3Hg}.I$; with somewhat less concentrated ammonia it yields white needles of the compound $NH_3.2HgI$ or $\overbrace{NH_3Hg}I + HgI$, and a red-brown powder consisting of iodide of tetramercurammonium with 2 eq. water $NHg_4I + 2HO$. The formation of this last compound is represented by the equation:

$$4HgI + 4NH_3 + 2HO = NHg_4I.2HO + 3NH_4I.$$

Iodide of tetramercurammonium is also formed by passing ammoniacal gas over mercuric oxy-iodide:

$$HgI.3HgO + NH_3 = NHg_4I.2HO + HO;$$

by digesting the chloride of tetramercurammonium in aqueous iodide of potassium (Rammelsberg); and by adding ammonia to a solution of iodide of mercury and potassium mixed with caustic potash (Nessler *):

$$4(HgI.KI) + NH_3 + 3KO = NHg_4I.2HO + 7KI + HO.$$

This last reaction affords an extremely delicate test for ammonia. A solution of iodide of mercury and potassium is prepared by adding iodide of potassium to a solution of corrosive sublimate, till a portion only of the resulting red precipitate is redissolved, then filtering, and mixing the filtrate with caustic potash. The liquid thus obtained produces a brown precipitate with a very small quantity of ammonia, either free or in the form of an ammoniacal salt. The precipitate is soluble in excess of iodide of potassium (Nessler).

* Chem. Gaz. 1856, 445. 463.

Mercuroso-mercuric iodide, Hg_4I_3 or $Hg_2I . 2HgI$.—This compound is obtained by precipitating a solution of mercurous nitrate with hydriodic acid or iodide of potassium, and collecting the precipitate on a filter after the green colour has changed to yellow; or by dissolving in aqueous iodide of potassium half as much iodine as it already contains, and adding the solution to a solution of mercurous nitrate. It is a yellow powder, which turns red when heated.

Cyanide of mercury, HgCy, 126 *or* 1575.—This salt is most easily obtained by saturating hydrocyanic acid with red oxide of mercury. To prepare the hydrocyanic acid required, the process of Winkler may be followed. Fifteen parts of ferrocyanide of potassium are distilled with 13 parts of oil of vitriol diluted with 100 parts of water, and the distillation continued by a moderate heat nearly to dryness. The vapour should be made to pass through a Liebig's condensing tube, and be afterwards received in a flask containing 30 parts of water. A portion of the condensed hydrocyanic acid is put aside, and the remainder mixed with 16 parts of oxide of mercury in fine powder, and well agitated till the odour of hydrocyanic acid is no longer perceptible. The solution is drawn off from the undissolved oxide of mercury, and the reserved portion of hydrocyanic acid mixed with it. The last addition is necessary to saturate a portion of oxide of mercury, which cyanide of mercury dissolves in excess. This operation yields 12 parts of the salt in question.

Cyanide of mercury may also be obtained by boiling 1 pt. of ferrocyanide of potassium for ten minutes with 2 pts. of neutral mercuric sulphate and 8 pts. of water, filtering the liquid, and leaving it to crystallise by cooling. The reaction may be represented by the equation:

$$K_2FeCy_3 + 3HgO = 3HgCy + 2KO + FeO.$$

A third method of preparing this compound is to heat the red oxide of mercury with about an equal weight of pure and finely pounded Prussian blue, and a large quantity of water, stirring the mixture frequently; then boil the filtrate with oxide of mercury to throw down the last portions of iron; and neutralise the excess of mercuric oxide in the liquid with hydrocyanic acid.

Cyanide of mercury crystallises in square prisms which are anhydrous, and resembles chloride of mercury in its solubility and poisonous qualities. The red oxide of mercury, even when dry, absorbs hydrocyanic acid, with formation of water and evolution of heat. The affinity of mercury for cyanogen appears to be particularly intense, oxide of mercury decomposing all the cyanides, even cyanide of potassium, and liberating potash. Cyanide of mercury is consequently not precipitated by potash. Nor is it decomposed by any acid, with the exception of hydrochloric, hydriodic, and hydrosulphuric acids. By a heat approaching to redness, cyanide of mercury is decomposed, and resolved into mercury and cyanogen gas. When exposed in the moist state to the action of chlorine in a dark place, it is converted into mercuric chloride and gaseous chloride of cyanogen:

$$HgCy + 2Cl = HgCl + CyCl.$$

But in strong sunshine, a different action takes place, attended with considerable rise of temperature, and yielding sal-ammoniac, mercuric chloride, a peculiar yellow oil, a small quantity of gaseous chloride of cyanogen, and a trace of carbonic acid (Serullas). When hydrocyanic acid is digested upon mercurous oxide, the mercuric cyanide dissolves, and metallic mercury is liberated.

Oxycyanide of mercury, $HgCy.HgO$, is produced as a white powder intermixed with the red oxide, when hydrocyanic acid of considerable strength (10 or 20 per cent.) is agitated with red oxide of mercury in large excess. It is sparingly soluble in cold water, but may be dissolved out by hot water, and crystallises on cooling in transparent, four-sided, acicular prisms. When heated gently, it blackens slightly, and then explodes (Johnston).*

Cyanide of mercury, digested upon red oxide of mercury, dissolves a large quantity of it, and forms, according to Kühn, a *tribasic cyanide of mercury*, HgCy . 3HgO, which is more soluble in water than the neutral cyanide, and crystallises with less facility in small acicular crystals.

Cyanide of mercury and potassium, KyCy . HgCy, is formed on dissolving cyanide of mercury in a solution of cyanide of potassium, and crystallises in regular octohedrons. Cyanide of mercury also forms crystallisable double salts with other cyanides, such as the cyanides of sodium, barium, calcium, magnesium, &c. It also combines with chlorides, bromides, iodides, and with several oxi-salts, such as chromate and formiate of potash, with which it forms the compounds $2(KO . CrO_3) + HgCy$ and $C_2HKO_4 . HgCy$.

Mercuric sulphate, $HgO . SO_3$; 148 *or* 1850.—This salt is formed by boiling 5 parts of sulphuric acid upon 4 parts of mercury, till the metal is converted into a dry saline mass. Mercuric sulphate is a white crystalline salt, neutral in composition, but, like most of the neutral salts of mercury, cannot exist in solution. Water decomposes it, forming a dense yellow subsulphate, and a solution of an acid sulphate. This subsulphate is known as *turbith mineral*, a name applied to it by the older chemists, because it was supposed to produce effects in medicine analogous to those of a root formerly employed, and known as convolvulus turpethum. The composition of turbith mineral is $3HgO . SO_3$ or $HgO . SO_3 + 2HgO$ (Kane). Solution of ammonia converts both the neutral sulphate and turbith mineral into a heavy powder, which Kane names *ammonio-turbith*, and finds to be $HgO . SO_3 + Hg . NH_2 + 2HgO$. It is, therefore, analogous in composition to the yellow powder produced by the decomposition of white precipitate, and may be regarded as a sulphate of tetramercurammonium with 2 eq. water: $NHg_4 . SO_4 + 2HO$.

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* Phil. Trans. 1839, p. 113.

Mercuric sulphites.—The neutral sulphite, $HgO . SO_2$, may be formed by precipitating the nitrate, $HgO . NO_5$, with an alkaline sulphate; but it is very unstable, and resolves itself spontaneously into mercuric sulphate and metallic mercury. The *basic sulphite*, $2HgO . SO_2$, is obtained by precipitating a solution of the basic nitrate, $2HgO . NO_5$, with an alkaline sulphite. It is a white, heavy powder, insoluble in water, and changing, when slightly heated, into mercurous sulphate; $2HgO . SO_2 = Hg_2O . SO_3$. Iodide of potassium converts it into red mercuric iodide (Péan de St. Gilles).* A *bisulphite*, $HgO . 2SO_2 + HO$, is obtained as a white crystalline powder by pouring a saturated solution of bisulphite of soda on solid mercuric chloride. It dissolves readily in water, and is decomposed by heat, whether in solution or in the solid state, with separation of metallic mercury (Wicke).† By treating mercuric chloride with a solution of neutral sulphite of potash, a double salt, $HgO . SO_2 + HO$, is obtained in small needle-shaped crystals, whose solution is neutral to test-paper. Similar salts are formed with the neutral sulphites of soda and ammonia. By treating mercuric chloride in excess with neutral sulphite of soda, the salt, $2(HgO.SO_2) + NaO.SO_2 + HO$, is obtained, which is alkaline to test-paper. The solutions of these double sulphites are precipitated by hydrosulphuric acid and soluble sulphides, but not by alkalies. (Péan de St. Gilles.)

Mercuric seleniate.—A hot aqueous solution of selenic acid forms with mercuric oxide prepared by precipitation, a soluble neutral seleniate, $HgO . SeO_3 + HO$, and a red insoluble basic salt, containing $2(3HgO . SeO_3) + HO$ (Körner).‡

Mercuric selenite.—Mercuric oxide forms with aqueous selenious acid, according to Berzelius, an insoluble neutral and a soluble acid selenite; according to Köhler, on the other hand, selenious acid does not form any soluble salt with mercuric oxide, but only a pale yellow amorphous salt, containing $7HgO.4SeO_2$.

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* Ann. Ch. Phys. [3], xxxvi. 80.

† Ann. Ch. Pharm. xcv. 176.

‡ Pogg. Ann. lxxxix. 146.

Nitrates of the red oxide of mercury, Mercuric nitrates.—The neutral nitrate cannot be crystallised, but it is formed in solution when chloride of mercury is precipitated by nitrate of silver. When red oxide of mercury is dissolved in nitric acid, or when the metal is dissolved in the same acid with ebullition, till a drop of the solution no longer occasions a precipitate in water containing a soluble chloride, a subnitrate is formed, crystallising in small prisms, which are deliquescent in damp air. Its composition is expressed by the formula $2HgO.NO_5+2HO$. It is the only crystallisable nitrate of this oxide. Decomposed by water, this salt yields a yellow subnitrate, which, after washing with warm but not boiling water, is $3HgO.NO_5+HO$. When the subnitrate is prepared by boiling water, it has a red colour, and probably consists of $6HgO.NO_5$ (Kane).

Nitrate of mercury yields several compounds when treated with ammonia. (*a.*) When a dilute and not very acid solution of that salt is treated in the cold, with weak solution of ammonia not added in excess, a pure milk-white precipitate appears, which is not granular, and remains suspended in the liquid for a considerable time. It was analysed by C. G. Mitscherlich, and to distinguish it from some other salts containing the same constituents, may be called *Mitscherlich's ammonia-subnitrate.* It contains $2HgO.NO_5 + HgNH_2$. (*b.*) The preceding compound is altered in its appearance by boiling water, and becomes much heavier and more granular, forming *Soubeiran's ammonia-subnitrate,* the composition of which is found by Kane to be $HgO.NO_5 + Hg.NH_2 + 2HgO$, or it resembles in constitution the bodies already described containing chlorine and sulphuric acid. This compound is also formed by decomposing a dilute solution of mercuric nitrate with a slight excess of ammonia (Soubeiran). (*c.*) A third compound, the *yellow crystalline ammonia-subnitrate,* was obtained by C. G. Mitscherlich by boiling the ammonia subnitrate (*a*) with excess of ammonia, and adding nitrate of ammonia, by which a portion of the powder is dissolved; the solution, as it cools and loses ammonia, yields small crystalline plates of a pale yellow colour. The constituents of this salt are $2HgO . NO_5$ and NH_3. Kane doubles its equivalent, and represents it as a compound of Soubeiran's salt with nitrate of ammonia, as it appears to be produced by the solution of the former salt in the latter, $(HgO . NO_5 + Hg . NH_2 + HgO) + NH_4O . NO_5$. (*d.*) Soubeiran's ammonia subnitrate (*a*) is dissolved in considerable quantity, when boiled in a strong solution of nitrate of ammonia, and the solution deposits, on cooling, small but very brilliant needles, which were observed and analysed by Kane. This salt, which may be called *Kane's ammonia subnitrate,* is decomposed by water, nitrate of ammonia dissolving, and Soubeiran's subsalt being left undissolved. It contains the elements of $3(NH_4O . NO_5)$ and $4HgO$. Kane believes that it is most likely to contain Soubeiran's subnitrate ready formed, which leaves two atoms of nitrate of ammonia and two atoms of water to be otherwise disposed of.*

These ammonia-nitrates, like the corresponding chlorides and sulphates, may be regarded as nitrates of mercurammoniums, containing one or more atoms of mercury in place of hydrogen. Thus, Mitscherlich's ammonia-subnitrate (*a*) is $N\overbrace{HHg_3} . NO_6 + HO$ = nitrate of trimercurammonium with 1 eq. water; Soubeiran's salt (*b*) is $NHg_4 . NO_6 + 2HO$ = nitrate of tetramercurammonium with 2 eq. water; the crystalline salt (*c*) is $N\overbrace{H_2Hg_2} . NO_6 + HO$ = nitrate of bimercurammonium with 1 eq. water; and (*d*) is a compound of (*b*) with nitrate of ammonia and water = $2(NH_4.NO_6)+2HO+(NHg_4.NO_6+2HO)$.

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* Trans. of the Royal Irish Academy, vol. xix. pt. i.; or, Ann. Ch. Phys. [2], lxxii. 225.

Nitrate of mercury forms an insoluble compound with sulphide of mercury, $HgO.NO_5+2HgS$, resembling the compounds of the sulphate and chloride with sulphide of mercury. It also forms double salts with iodide and cyanide of mercury.

Alloys of mercury or amalgams.—Mercury combines with a great number of metals, forming compounds called *amalgams*, which are liquid or solid according as the mercury or the other metal predominates. A very small quantity of a foreign metal suffices to impair the fluidity of mercury in a very great degree. All amalgams are decomposed by heat, the mercury volatilising and the other metal remaining.

The union of mercury with potassium and sodium is attended with considerable disengagement of heat; the resulting amalgams are of a pasty consistence, and decompose water. The amalgams of tin and lead, when heated till they are quite liquid, and then left to cool slowly, yield solid crystalline amalgams of definite constitution. An amalgam of silver, Hg_2Ag, is found native in the form of regular dodecahedrons.

An amalgam of tin is used for *silvering* glass. For this purpose a sheet of tinfoil is laid on a horizontal table, and mercury poured over the whole surface, so as to form a layer about 1-5th or 1-6th of an inch thick. The plate of glass is then slid along the surface in such a manner as to cut this layer in halves horizontally, which prevents the introduction of air-bubbles. The glass is then loaded with weights, so as to press out the excess of mercury; and after a few days, the surface is found to be covered with a closely-adhering layer of an amalgam containing about 5 parts of tin to 1 of mercury.

Mercury combines very readily with bismuth. An amalgam obtained by heating a mixture of 497 parts of bismuth, 810 lead, 177 tin, and 100 mercury, is very well adapted for injecting anatomical preparations: it is solid at ordinary temperatures, and has a silvery lustre, melts at 171·5 (Fah.), and solidifies at 140°. An amalgam of lead and tin, sometimes also containing bismuth, is used for covering the cushions of electrical machines.

ESTIMATION OF MERCURY, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Mercury is generally estimated in the metallic state; sometimes, however, as sulphide, HgS, or as dichloride, Hg_2Cl. To separate it from its compounds in the metallic state, it may be distilled with quicklime, in a tube of hard glass sealed at one end. Into this tube is introduced, first a layer of carbonate of lime, about an inch long; then the mixture of the substance with quicklime; lastly, a layer of quicklime about two inches long, and a plug of asbestos to keep the lime in its place. The open end of the tube is next drawn out into a narrow neck, and bent at an obtuse angle. The tube is laid in a combustion-furnace, the same as that which is used for organic analysis (I, 373), the neck being turned downwards and made to pass into a narrow-mouthed bottle containing water, so as to terminate just above the surface of the water. The tube is then gradually heated by laying pieces of red-hot charcoal round it, beginning at the part near the neck, containing the pure quicklime. This portion having been brought to a full red heat, the heat is carefully extended towards the middle part, to decompose the compound and volatilise the mercury: any portion of the compound that may volatilise undecomposed, will be decomposed in passing over the red-hot lime at the end. Lastly, the back part of the tube containing the carbonate is heated, so as to evolve carbonic acid gas and sweep out all the mercury vapour contained in the tube. The quantity of carbonic acid thus evolved may be increased by mixing the carbonate of lime with bicarbonate of soda. The mercury condenses under the water in the bottle, which must be kept cold. The water is poured off as completely as possible; the mercury transferred to a weighed porcelain crucible; the greater part of the water which still adheres to it removed by means of blotting-paper; the drying completed over sulphuric acid; and the mercury finally weighed.

Mercury may also be precipitated from its solutions in the metallic state by protochloride of tin, or by phosphorous acid; the solution then decanted; the mercury washed with water; and dried in the manner just described.

Mercury is also frequently precipitated from its solutions, as a sulphide, by hydrosulphuric acid. In that case, if the precipitate consists of the pure protosulphide, HgS, as when it is thrown down from a solution of corrosive sublimate, the precipitate may be simply collected on a weighed filter, washed, dried over the water-bath, weighed, and the quantity of mercury thence determined. But if, as is generally the case, the precipitate also contains free sulphur, as when it is thrown down from a solution containing a ferric salt, or a considerable excess of nitric acid,—or if it be precipitated in conjunction with the sulphides of other metals, then the mercury must be separated from it by distillation with lime, as above described. Or again, the mixture of sulphides may be converted into chlorides by gentle heating in a stream of chlorine gas, the volatile chloride of mercury passed into water, and the mercury precipitated from the solution by protochloride of tin.

The precipitation of mercury in the form of dichloride is best effected by means of hydrochloric acid and formiate of potash or soda. If the mercury is contained in an alloy, the alloy must be dissolved in aqua-regia; if it is contained in solution in the form of mercuric nitrate, hydrochloric acid must be added, the solution, in either case, nearly neutralised with potash, formiate of potash or soda then added, and the whole exposed for some days to a temperature between 140° and 176° F. (at the boiling heat, the mercury would be reduced to the metallic state.) The dichloride then precipitates, and must be collected on a weighed filter, washed, dried at a gentle heat, and weighed.

The quantity of *mercurous oxide* present in a solution may also be determined by precipitation with hydrochloric acid. The solution must, however, be very dilute, and be kept cool; it must also contain but a very small quantity of free nitric acid, as a larger quantity would convert the dichloride of mercury into protochloride. To determine the proportions of mercurous and mercuric oxide, when they exist together in solution, the mercurous oxide is first precipitated with hydrochloric acid, and the remaining mercury by protochloride of tin or hydrosulphuric acid.

Mercury may be separated from all other metals, except arsenic and antimony, by its superior volatility. When it exists in the form of an amalgam, the compound is simply heated, and the quantity of mercury determined by the loss of weight. If it exists as an oxide, chloride, &c., combined with compounds of other metals, it may be separated by distillation with quicklime, as above described. Its separation from the *alkalies* and *earths*, and from *uranium*, *manganese*, *nickel*, *cobalt*, *iron*, *zinc*, and *chromium*, may also be effected by precipitation with hydrosulphuric acid. From *bismuth* and *cadmium* it may be separated by reduction with protochloride of tin; from *copper*, by mixing the solution with excess of cyanide of potassium, and passing hydrosulphuric acid through the liquid, whereby the mercury is precipitated as sulphide, while the copper remains dissolved; from *lead*, by precipitating that metal with sulphuric acid; also by treating the solution with excess of cyanide of potassium, which precipitates the lead, but not the mercury. From *arsenic*, *tin* and *antimony*, mercury is separated by the solubility of the sulphides of those metals in sulphide of ammonium.

SECTION II.

SILVER.

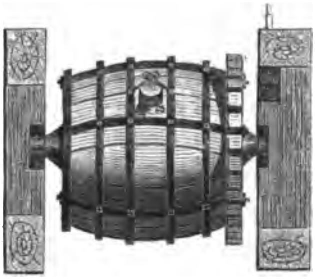
Eq. 108, *or* 1350; Ag (*argentum*).

This metal is found in various parts of the world, and occurring often in the metallic state, and being easily melted, must have attracted the attention of mankind at an early period. Before the discovery of America, the silver mines of Saxony were of considerable importance; but the silver mines of Mexico and Peru far exceed in value the whole of the European and Asiatic mines, the former having furnished during the last three centuries, according to Humboldt, 316 millions of pounds troy of pure silver.

A considerable quantity of silver is obtained from ores of lead by cupellation, as described under that metal. From argentiferous copper ores also the silver is extracted by a process called *liquation*, which consists in fusing the *coarse copper* (p. 93.) with three times its weight of lead; a mixture of two alloys is then obtained, the more fusible of which, containing the greater part of the lead and nearly all the silver, is separated by the application of a moderate heat, and yields the silver by cupellation.

Native silver, which is in the form of threads or thin leaves, is separated from the gangue or accompanying rock, by *amalgamation*, a process which is also followed in the treatment of the most frequent ore of silver, the sulphide, when it is not accompanied by sulphide of lead. At Freiberg, in Saxony, the sulphide of silver, ground to powder, is roasted in a reverberatory furnace with 10 per cent. of chloride of sodium, by which the silver is converted into chloride. It is then introduced into barrels (fig. 19.), with water, iron, and a quantity of metallic mercury, and the materials kept in a state of agitation for eighteen hours by the revolution of the barrels on their axes. The chloride of silver, although insoluble, is reduced to the metallic state by the iron, and chloride of iron is produced, while the silver forms a fluid compound with the mercury. By adding more water, and turning the barrels more slowly, the fluid amalgam separates and subsides. It is drawn off and subjected to pressure in a chamois leather bag, the mercury passing through the leather, while a soft amalgam of silver remains in the bag. The mercury is afterwards separated from this amalgam by a species of distillation, *per descensum*, and the silver remains.

Fig. 19.



In South America, where fuel is scarce, a different process is adopted. The ore, in a finely divided and moist condition, is exposed for a considerable time to the successive action of common salt, sulphate of copper (obtained by roasting copper pyrites), and mercury, the materials being spread on a paved floor, and trodden by men or horses to effect an intimate mixture; and the silver amalgam thus obtained is separated from the exhausted ore by washing with water. In this process, the chloride of sodium and sulphate of copper form sulphate of soda and protochloride of copper. The latter gives up chlorine, converting part of the silver into chloride, and separates the sulphur, provided an excess of chloride of sodium is present to dissolve the dichloride of copper as it forms. The dichloride of copper then acts upon another portion of the sulphide of silver, forming disulphide of copper and chloride of silver: $Cu^2Cl + AgS = Cu^2S + AgCl$. The chloride of silver thus produced, dissolves in the chloride of sodium, and is decomposed by the mercury subsequently added, yielding calomel and metallic silver. This process is always attended with considerable loss of mercury, which however may be diminished by the previous addition of iron. Mr. P. Johnston proposes to diminish the loss of mercury, as soluble chloride, which occurs in this process, by using an amalgam of zinc and mercury, instead of pure mercury.

Silver is obtained free from other metals, and in a state of purity, for chemical and other purposes, by the following processes: — 1. The metal is dissolved in pure nitric acid slightly diluted, and precipitated by a solution of chloride of sodium, the salts of the other metals present remaining in solution. The insoluble chloride of silver, thus obtained, is thoroughly washed upon a filter with hot water and dried. A quantity of carbonate of potash, equal to twice the weight of the silver, is then fused in a crucible, and the chloride of silver gradually added to it, whereupon chloride of potassium is formed, and carbonic acid and oxygen escape with effervescence. The crucible is then exposed to a heat sufficient to fuse the reduced silver, which subsides to the bottom.—2. The mode of separating silver from the common metals, in the ordinary practice of assaying, is, like many metallurgic operations, an exceedingly elegant and refined process. A portion of the silver alloy, the *assay*, is fused with several times its weight of pure lead (an alloy of 1 copper and 15 silver with 96 lead, for instance) upon a bone-earth cupel, which is supported in a little oven or muffle, heated by a proper furnace. Air being allowed access to the assay, the lead is rapidly oxidated, and its highly fusible oxide imbibed, as it is produced, by the porous cupel. The disposition of copper and other common metals to oxidate is increased by the presence of the lead; and their oxides, which form fusible compounds with oxide of lead, are removed in company with the latter. When the foreign metal is almost entirely removed, the assay is observed to become rounder and more brilliant, and the last trace of fused oxide occasions a beautiful play of prismatic colours upon its surface, after which the assay becomes, in an instant, much whiter, or *flashes*, an indication that the cupellation is completed.

Pure silver may also be obtained from an alloy containing only silver and copper, by precipitating the two metals with excess of carbonate of soda with the aid of heat, boiling the precipitate for about ten minutes with a solution of grape-sugar, whereby the copper is reduced to the state of red oxide, and the silver to the metallic state, and treating the moist precipitate with a hot solution of carbonate of ammonia: the copper then dissolves, and pure silver remains.

Pure silver is the whitest of the metals, and susceptible of the highest polish; when granulated by being poured from a height of a few feet into water, its surface is rough, but its aspect peculiarly beautiful. It crystallises in cubes and regular octohedrons, both from a state of fusion and by precipitation from solution. Silver is in the highest degree ductile and malleable; its density varies between 10·474 and 10·542; it fuses at 1873°. When in the liquid state, it is capable of absorbing oxygen gas from the air, which is discharged again in the solidification of the metal, and gives rise to a sort of vegetation upon its surface, or even occasions the projection of small portions of the silver to a distance, an accident which is known in assaying as the *spitting* of the metal. Gay-Lussac observed, that when a little nitre was thrown upon the surface of melted silver in a crucible, and the whole kept in a state of fusion for half an hour, a very considerable absorption of oxygen took place. When the crucible was removed from the fire and quickly placed under a bell-jar filled with water, which can be done without danger, the silver discharged a quantity of oxygen equal to 20 times its volume. This property is possessed only by pure silver, and does not appear at all in silver containing 1 or 2 per cent. of copper. As oxide of silver is reduced by a red heat, the absorption of the oxygen by the fluid metal must be a phenomenon of a different nature from simple oxidation.

Silver does not combine with the oxygen of the air at the usual temperature, nor even when heated; the tarnishing of polished silver in air is occasioned by the formation of sulphide of silver. Silver does not dissolve in any hydrated acid, by substitution for hydrogen, but on the contrary is displaced from solution in an acid by hydrogen, and precipitated in the metallic state. This metal is also precipitated by mercury and by all the more oxidable metals. Its salts are reduced at the usual temperature by sulphate of iron, the protoxide in which is converted into sesquioxide. But if the ferric sulphate is boiled upon the precipitated silver, the latter is dissolved again, and oxide of silver and protoxide of iron reproduced. Silver, however, is oxidated when fused or heated strongly in contact with substances for which oxide of silver has a great affinity, as with a siliceous glass, and stains the glass yellow. It is oxidated by concentrated sulphuric acid, with evolution of sulphurous acid. Silver is readily dissolved by nitric acid, at a gentle heat, and with much violence, at a high temperature, nitrate of silver being formed, and nitric oxide escaping. Silver combines in three proportions with oxygen, forming a suboxide, Ag_2O, a protoxide AgO, and a peroxide, AgO_2.

Suboxide of silver, Ag_2O.—Pure protoxide of silver is completely reduced to the state of metal by hydrogen gas, at 212°; but the oxide contained in citrate of silver loses only half its oxygen under the same circumstances, the suboxide being formed and remaining in combination with one half of the citric acid of the former salt. The aqueous solution of the suboxide salt is dark brown, and the suboxide is precipitated black from it by potash. When the solution of the subsalt is heated, it becomes colourless, and metallic silver appears in it. The salt dissolves with a brown colour in ammonia. Several other salts of silver, containing organic acids, comport themselves in the same way as the citrate, when heated in hydrogen.* A solution of protoxide of silver in ammonia deposits on exposure to the air, a grey suboxide, containing 108 parts of silver to 5·4 parts oxygen. When heated, it gives off oxygen and leaves metallic silver (Faraday).†

Protoxide of silver, AgO, 116 *or* 1450.—This oxide is thrown down, when potash or lime-water is added to a solution of nitrate of silver, as a brown powder, which becomes of a darker colour when dried. The powder was found to be anhydrous by Gay-Lussac and Thénard; its density is 7·143, according to J. Herapath; 7·250, according to P. Boullay; 8·2558, according to Karsten. Oxide of silver is decomposed by light, or at a red heat, into oxygen gas and metallic silver. Hydrogen reduces it even at 212°. It is also reduced by an aqueous solution of phosphorous acid. When recently precipitated, it is decomposed by aqueous sulphurous acid, yielding metallic silver and sulphate of silver; but the decomposition is only partial, even when aided by heat. When immersed in water, it is reduced by zinc, cadmium, tin, and copper, but not by iron or mercury. In an aqueous solution of hypochlorous acid, it is converted into chloride of silver, oxygen being evolved together with a small quantity of chlorine.

Oxide of silver is a powerful base, and forms salts, several of which have been found isomorphous with the corresponding salts of soda. Like oxide of lead, it dissolves to a small extent in pure water free from saline matter, and the solution has an alkaline reaction. Oxide of silver is not dissolved by solutions of the hydrates of potash and soda. Its salts are precipitated black by *hydrosulphuric* acid and *alkaline sulphides*. When treated with *hydrochloric* acid or a *soluble chloride*, they yield a white curdy precipitate, the chloride of silver, which soon becomes purple, if exposed, while moist, to the direct rays of the sun. This precipitate is not dissolved by nitric acid, but is dissolved by ammonia in common with most of the insoluble salts of silver. This precipitate is visible, according to Lassaigne, even in solutions containing only 1 part of silver in 800,000 parts of liquid. In a solution containing 1 part of silver in 200,000 parts, hydrochloric acid or common salt produces a slight turbidity; with 1 part of silver in 400,000, the same reagents produce a scarcely perceptible opalescence; and if the proportion of liquid amounts to 800,000 parts, the opalescence does not show itself for a quarter of an hour. *Hydrobromic acid* and soluble metallic *bromides*, added to solutions of silver-salts, throw down all the silver in the form of yellowish white bromide, insoluble in nitric acid, and sparingly soluble in ammonia. *Hydriodic* acid and soluble *iodides* form a pale yellow precipitate of iodide of silver, likewise insoluble in nitric acid, and still less soluble in ammonia. *Hydrocyanic* acid and soluble *cyanides* throw down a white precipitate of cyanide of silver, easily soluble in ammonia, insoluble in cold dilute nitric acid, but dissolved by strong nitric acid at a boiling heat, with evolution of nitric oxide. *Ammonia* added in very small quantity to perfectly neutral silver-salts, produces a slight brown precipitate of oxide of silver, easily soluble in excess; but if the solution contains excess of acid, ammonia produces no precipitate. *Potash* added to the ammoniacal solution produces a white precipitate, provided the excess of ammonia be but small. The *fixed alkalies* form, in neutral or acid solutions of silver-salts, a brown precipitate of oxide of silver, insoluble in excess. *Alkaline carbonates* precipitate white carbonate of silver, soluble in ammonia and carbonate of ammonia. *Ordinary tribasic phosphate of soda* forms a yellow precipitate; *pyrophosphate* and *metaphosphate of soda* form white precipitates. *Chromate of potash* forms a dark crimson precipitate of chromate of silver. *Alkaline arsenites* form a canary-yellow precipitate of arsenite of silver. *Oxalic acid* forms a white pulverulent precipitate of oxalate of silver. Silver is precipitated from its solutions in the metallic state by *phosphorus, phosphorous acid, phosphuretted hydrogen,* and *sulphurous acid* (imperfectly); by various *metals,* viz., zinc, cadmium, tin, lead, iron, manganese, copper, mercury, bismuth, tellurium, antimony, and arsenic; also by protoxide of uranium, hydrated protoxide of manganese, and protoxide of tin; and by various *organic substances* at a boiling heat, *e.g.*, charcoal, sugar, aldehyde, formic acid, tincture or infusion of galls, and volatile oils. Many organic substances added to a solution of nitrate of silver mixed with excess of ammonia, throw down metallic silver in the form of a beautiful specular film lining the sides of the vessel. This effect is produced by aldehyde, saccharic acid, salicylous acid, pyromeconic acid, and various essential oils. A mixture of oil of cinnamon and oil of cloves is found to produce an exceedingly brilliant speculum, and has indeed been used for silvering mirrors in place of the ordinary process with tin and mercury; it is particularly adapted for silvering curved surfaces. A very bright and regular specular surface is also produced by adding a solution of milk-sugar to an ammoniacal solution of nitrate of silver mixed with caustic potash or soda; the precipitation then takes place without the application of heat (Liebig).*

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* Ann. Ch. Pharm. xxx. 1.

† Ann. Ch. Phys. [2], ix. 107.

Oxide of silver combines with ammonia and forms the fulminating *ammoniuret of silver,* a substance of a dangerous character from the violence with which it explodes. The ammoniuret may be formed by digesting newly precipitated oxide of silver in strong ammonia, or more readily by dissolving nitrate of silver in ammonia, and precipitating the liquor by potash in slight excess. If this substance be pressed by a hard body, while still moist, it explodes with unequalled violence; when dry, the touch of a feather is often sufficient to cause it to fulminate. The explosion is obviously occasioned by the reduction of the silver from the combination of its oxygen with the hydrogen of the ammonia, and the evolution of nitrogen gas.

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* Ann. Ph. Pharm. xcviii. 132.

Sulphide of silver, AgS, 124 *or* 1550.—Sulphur and silver may be combined together by fusion; the excess of sulphur escapes, and at a high temperature the sulphide melts; it forms, on cooling, a crystalline mass. This compound has a lead-grey colour and metallic lustre. It is so soft that it may be cut with a knife, and is malleable. The sulphide of silver is also remarkable for conducting electricity, like a metal, when warmed. The same compound occurs in nature, sometimes crystallised in octohedrons with secondary faces. This sulphide is particularly interesting from being isomorphous with the subsulphide of copper, AgS with Cu_2S (page 144). These two sulphides replace each other in indeterminate proportions in several double sulphides of silver and other metals, as in *polybasite* and *fahl-ores*, the composition of which may be expressed by the following formulæ, the symbols placed above each other representing constituents, of which either the one or the other may be present:

$$\text{Polybasite} \quad . \quad 9\genfrac{}{}{0pt}{}{Cu_2S}{AgS} + \genfrac{}{}{0pt}{}{SbS_3}{AsS_3}$$

$$\text{Fahl-ores} \quad \left(4\genfrac{}{}{0pt}{}{ZnS}{FeS} + \genfrac{}{}{0pt}{}{SbS_3}{AsS_3}\right) + 2\left(4\genfrac{}{}{0pt}{}{AgS}{Cu_2S} + \genfrac{}{}{0pt}{}{SbS_3}{AsS_3}\right).$$

Chloride of silver, AgCl, 143·5 *or* 1793·75.—This salt contains in 100 parts, 24·69 parts of chlorine, and 75·31 parts of silver. It is found native as *horn-silver*, in translucent cubes or octohedrons of a greyish-white colour, and specific gravity 5·55. The same compound is also thrown down as a white precipitate, at first very bulky and curdy, when hydrochloric acid or a soluble chloride is added to any soluble salt of silver, except the hyposulphite. It is wholly insoluble in water, and the most minute quantity of hydrochloric acid contained in water may be detected by adding to it a drop of a solution of nitrate of silver (p. 336.) Hydrochloric acid, when concentrated, dissolves chloride of silver, which crystallises from it in octohedrons, when the solution is evaporated. This salt dissolves easily in solution of ammonia, and crystallises also as the ammonia evaporates. When heated, it fuses at about 500°, forming a transparent yellowish liquid, which becomes, after cooling, a mass that may be cut with a knife, and has considerable resemblance to horn: a property to which it was indebted for the name of *horn-silver*, applied to it by the older chemists. It is not volatile. Chloride of silver is not affected by a concentrated solution of potash. It is easily reduced to the state of metal by zinc or iron with water. Chloride of silver may be dissolved out in this way by means of zinc and acidulated water, from a porcelain crucible in which it has been fused. To obtain pure silver by this mode of reduction, it is necessary to use zinc free from lead, otherwise that metal, not being dissolved by the sulphuric acid, remains mixed with the silver. A better mode of reduction is to boil the chloride of silver with an equal weight of starch-sugar and a solution of one part of carbonate of soda in three parts of water (Böttger). The chloride and other salts of silver acquire a dark colour when exposed to light; chlorine escapes, and a portion of the salt appears to be reduced to the metallic state, as the blackened surface conducts electricity. According to Wetzlar, the black substance contains an inferior chloride of silver, and is not attacked by nitric acid, or soluble in ammonia. It has also been supposed that the blackening is due, not to any chemical decomposition, but merely to a change in the state of aggregation of the particles. It appears, however, from some recent experiments by Dr. F. Guthrie, that the chloride is completely decomposed and metallic silver separated, even in presence of free nitric acid. Paper charged with chloride of silver is very sensitive to the impression of light, and is the material used for positive photographs, the unaltered chloride being afterwards dissolved out by a solution of hyposulphite of soda.

One hundred parts of chloride of silver absorb 17·9 parts of ammoniacal gas, forming the compound, $3NH_3 . 2AgCl$, or $\mathrm{N}\left.\begin{matrix}\overbrace{\mathrm{H(NH_4)_2Ag}}\\ \mathrm{Ag}\end{matrix}\right\}\mathrm{Cl_2}$. This compound gives off its ammonia in the air. Chloride of silver is dissolved by concentrated and boiling solutions of the chlorides of potassium, sodium, and ammonium, and, on cooling, a double salt is deposited in crystals, generally cubes. Chloride of silver is also dissolved by cyanide of potassium, and the solution yields a double salt by evaporation (Liebig).

Bromide of silver, AgBr, 188 *or* 2350.—This salt consists in 100 parts, of 42·56 bromine and 57·44 silver. It is found native in Mexico and in Bretagne; sometimes in small amorphous masses, sometimes in greenish-yellow octohedral crystals. It is insoluble in water, and falls as a precipitate which is white at first, but becomes pale yellow when collected. When fused and cooled, it yields a mass of a pure and intense yellow colour. It has most of the properties of chloride of silver, but dissolves very sparingly in ammonia.

Iodide of silver, AgI, 234·36 *or* 2929·5.—This salt contains in 100 parts, 53·87 of iodine and 46·13 of silver. It is found native, sometimes in regular hexagonal prisms. It is insoluble in water, like the chloride, and is prepared in a similar manner by precipitation, but is distinguished from that salt by its colour, which is pale yellow, by the difficulty with which it is dissolved in ammonia, being even less soluble than the bromide, and by being blackened more slowly by the action of light. According to Martini, 2500 parts of ammonia, of density 0·960, are required to dissolve one part of iodide of silver. It is soluble to a large extent, at the boiling temperature, in concentrated solutions of the alkaline and earthy iodides, and forms with them double salts.

Silver is rapidly dissolved by hydriodic acid, with evolution of hydrogen. If the action is assisted by heat, the solution deposits, on cooling, a colourless crystalline salt, resembling nitrate of silver, but decomposing as soon as it is separated from the liquid: it appears to consist of an iodide of silver and hydrogen. The mother-liquor, when left to itself, deposits iodide of silver in large regular six-sided prisms, resembling the native iodide (H. Ste.-Claire Deville).*

Fluoride of silver, AgF, is obtained by dissolving the oxide or carbonate in hydrofluoric acid. It is very soluble in water, and is partly decomposed by evaporation.

Cyanide of silver, $AgCy$; 134 *or* 1675.—This salt contains, in 100 parts, 19·41 cyanogen and 80·59 silver. It falls as a white powder when hydrocyanic acid is added to a solution of nitrate of silver. It is distinguished from chloride of silver by dissolving in concentrated nitric and sulphuric acids, when heated. It is readily decomposed by hydrochloric acid, and yields hydrocyanic acid, 100 parts of cyanide of silver giving 20·36 parts of hydrocyanic acid. It is decomposed by a red heat, giving off half its cyanogen and leaving paracyanide of silver, Ag_6Cy_3. Cyanide of silver is dissolved by cyanide of potassium, and other soluble cyanides. The double cyanide of potassium and silver crystallises in octohedrons, $KCy \,.\, AgCy$.

Carbonate of silver, $AgO.CO_2$, is a white insoluble powder.

Sulphate of silver, $AgO.SO_3$; 156 *or* 1950.—Obtained by dissolving silver, with heat, in concentrated sulphuric acid, or by precipitating a solution of nitrate of silver with sulphate of potash. It is soluble in 88 times its weight of boiling water, and crystallises, on cooling, in the form of anhydrous sulphate of soda. This salt is highly soluble in ammonia, and gives, by evaporation, an ammoniacal sulphate of silver in fine transparent crystals, which are persistent in air; $AgO.SO_3 + 2NH_3$, or $NH_2\overbrace{(NH_4)Ag}\,.\,SO_4$. Chromate and seleniate of silver form analogous compounds with ammonia, which are all isomorphous. The bichromate of silver is also isomorphous with bichromate of soda.

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* Compt. rend. xlii. 894.

Hyposulphate of silver, $AgO.S_2O_5$, is soluble in water, and crystallises in the same form as hyposulphate of soda. It crystallises also with ammonia, as $AgO.S_2O_5 + 2NH_3$, or $N\,\overbrace{H_2(NH_4)Ag}\,.\,S_2O_6$.

Hyposulphite of silver, $AgO.S_2O_2$.—Hyposulphurous acid appears to have a greater affinity for oxide of silver than for any other base. Oxide of silver decomposes the alkaline hyposulphites, liberating one-half of their alkali, and forming a double hyposulphite of the alkali and silver. These double salts are best prepared by adding chloride of silver in small portions to the soluble hyposulphite of potash, soda, ammonia, or lime in the cold, till the liquid is saturated; after which, the solution is filtered, and mixed with a large quantity of alcohol, which precipitates the double salt; the potash and soda salts are crystallisable. Herschel considers the double salts obtained in this manner as probably containing one eq. of hyposulphite of silver to two eq. of the other hyposulphite. The solution of one of these double salts dissolves more oxide of silver, and forms a double salt, which is believed to contain single equivalents of the salts, and precipitates as a white crystalline, pulverulent, bulky mass. The second compound is sparingly soluble in water, but dissolves in ammonia, and communicates to the liquor an intensely sweet taste.

The hyposulphite of silver itself is an insoluble substance; it is prone to undergo decomposition, changing spontaneously into sulphate and sulphide of silver. When to a dilute solution of nitrate of silver, a dilute solution of hyposulphite of soda is added by small quantities, a white precipitate of hyposulphite of silver falls, which dissolves again in a few seconds, from the formation of the soluble double hyposulphite of soda and silver. When enough of hyposulphite of soda has been gradually added to render the precipitate permanent, without, however, decomposing the whole silver salt, a flocculent mass is obtained of a dull grey colour, which is permanent. The liquor contains much hyposulphite of silver, and has an intensely sweet taste, not at all metallic; the silver is not precipitated from it by hydrochloric acid or the chlorides. An excess of hyposulphite of soda destroys the precipitated hyposulphite of silver, converting it into sulphide of silver.

Nitrate of silver, $AgO . NO_5$; 170 *or* 2125.—When a piece of pure silver is suspended in nitric acid, it dissolves for a time without effervescence at a low temperature, nitrous acid being produced, which colours the liquid blue; but if heat be applied or the temperature allowed to rise, then the metal dissolves with violent effervescence, from the escape of nitric oxide. The nitrate of silver crystallises on cooling in colourless tables, which are anhydrous. It is soluble in 1 part of cold, in ½ part of hot water, and in 4 parts of boiling alcohol. The solution of this salt does not redden litmus paper, like most metallic salts, but is exactly neutral. Nitrate of silver fuses at 426°, and forms a crystalline mass on cooling; it is cast into little cylinders for the use of surgeons. It is sometimes adulterated in this state with nitrate of potash, which may be detected by the alkaline residue which the salt then leaves when heated before the blowpipe,—or with nitrate of lead, in which case the solution of the salt is precipitated by iodide of potassium, of a full yellow colour. When applied to the flesh of animals, it instantly destroys the organisation and vitality of the part. It forms insoluble compounds with many kinds of animal matter, and is employed to remove it from solution. When organic substances, to which a solution of nitrate of silver has been applied, are exposed to light, they become black from the reduction of the oxide of silver to the metallic state. A solution of nitrate of silver in ether is employed to dye the hair black. One part of nitrate of silver and 4 parts of gum arabic dissolved in 4 parts of water, and blackened with a small quantity of Indian ink, form the indelible marking ink used to write upon linen. The part of the linen to be marked should be first wetted with a solution of carbonate of soda and dried, and the writing should be exposed to the light of the sun. For this ink, which is expensive, another liquid has been substituted by bleachers, namely coal tar, made sufficiently thin with naphtha to write with, which is found to resist chlorine, and to answer well as a marking ink.

A strong solution of nitrate of silver absorbs two equivalents of ammoniacal gas, and forms the crystallisable *Ammoniacal nitrate of silver*, $AgO . NO_5 + 2NH_3 = N\,\overbrace{H_2(NH_4)Ag} . NO_6$. The dry nitrate in powder absorbs three atoms of ammonia, $AgO.NO_5 + 3NH_3 = N\,\overbrace{H(NH_4)_2Ag} . NO_6$.

Nitrate of silver forms a double salt with nitrate of the red oxide of mercury, which crystallises in prisms. Nitrate of silver and cyanide of mercury also form a double salt, when hot solutions of them are mixed: $AgO.NO_5 + 2HgCy + 8HO$. Cyanide of silver is soluble in a boiling solution of nitrate of silver, and forms a crystalline compound, $AgO . NO_5 + 2AgCy$, which is decomposed by water.

Nitrite of silver, $AgO . NO_3$; 154 or 1925. — Nitrate of soda is fused at a red heat, till it is wholly converted into nitrite by loss of oxygen; the latter salt then begins to give off nitrous acid, and a small portion of the salt dissolved in water will be found to precipitate silver brown. The fusion is then interrupted, the salt dissolved in boiling water, precipitated by nitrate of silver, and filtered while still very hot. The nitrite of silver, which requires 120 times its weight of water at 60° to dissolve it, is precipitated as the solution cools. The other nitrites are prepared by rubbing this salt in a mortar with chlorides taken in equivalent quantities. It appears from experiments of Proust, that two subnitrites of silver exist, one soluble and the other insoluble.

Acetate of silver, which is soluble in 100 times its weight of cold water, is precipitated when acetate of copper is mixed with a concentrated solution of nitrate of silver. It crystallises from solution in boiling water in anhydrous needles.

Oxalate of silver is an insoluble powder. A double *oxalate of potash and silver* is formed by saturating binoxalate of potash with carbonate of silver. It is very soluble, and forms rhomboidal crystals, which are persistent in air.

Peroxide of silver.—A superior oxide of silver is deposited upon the positive pole or zincoid of a voltaic battery in a weak solution of nitrate of silver, in the form of needles of 3 or 4 lines in length, which are black and have a metallic lustre, while metallic silver is, at the same time, deposited in crystals upon the negative pole or chloroid. The former crystals are converted by sulphuric acid into oxide of silver and oxygen, and yield with hydrochloric acid, chloride of silver and chlorine. According to Fischer, whose observations are confirmed by L. Gmelin, the peroxide prepared as above from nitrate of silver always retains nitric acid, and if prepared in a similar manner from the sulphate, it always retains sulphuric acid.*

Alloys of silver.—Silver may be readily alloyed with most metals. It combines by fusion with iron, from which it cannot be separated by cupellation. Native silver is always associated with gold; the two metals are found crystallised together in all proportions in the same cubic or octohedral crystals. Gold may be detected in a silver coin, by dissolving the latter in pure nitric acid, when a small quantity of black powder remains, which after being washed with water, will be found to dissolve in nitro-hydrochloric acid, giving a yellow solution, in which protochloride of tin produces a precipitate of the purple powder of Cassius. Pure silver, being very soft, is always alloyed in coin and plate, with a certain quantity of copper, to make it harder. The standard silver of England is an alloy of 222 pennyweights of silver with 18 pennyweights of copper., or it contains 92·5 per cent. of silver. The standard of the Spanish dollar, of the French and most other coinages, is 90 per cent. of silver. The alloy of silver and copper of greatest stability consists of 71·9 silver, and 28·1 copper, and corresponds with the formula $AgCu_4$.*

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* Gmelin's Handbook, Translation, vi. 145.

ESTIMATION OF SILVER, AND METHODS OF SEPARATING IT FROM OTHER METALS.

Silver, when in the state of solution, is always estimated as chloride. The solution, if not already acid, is slightly acidulated with nitric acid; the silver precipitated with hydrochloric acid, and the liquid placed for some hours in a warm situation to cause the precipitated chloride of silver to settle down. The precipitate is collected on a filter, which should be as small as possible, washed with water, and dried at 212°. It must then be separated as completely as possible from the filter; introduced into a porcelain crucible, previously weighed; the filter burnt to ashes outside the crucible; the ashes added to the contents of the crucible; and the whole strongly heated over a lamp till the chloride of silver is brought to a state of tranquil fusion, after which it is left to cool and weighed. It contains 75·26 per cent. of silver. This mode of estimation is affected with an error, arising from the partial reduction of the chloride of silver by the organic matter of the filter. The error thus occasioned is but slight when the process is well conducted, and may always be obviated by treating the fused chloride after cooling with nitric acid to dissolve the reduced silver; then adding hydrochloric acid, evaporating to dryness, and again fusing the residue. Another mode of proceeding is to collect the chloride of silver on a weighed filter, and dry it in an oil-bath, at about 300° F. The chloride may also be washed by decantation, and the use of a filter avoided altogether; but the washing requires very careful manipulation.

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* Levol, Ann. Ch. Phys. [3], xxxvi. 220.

The quantity of silver in a solution may also be determined by precipitating it with a solution of chloride of sodium of known strength. The solution of chloride of sodium is made of such a strength that a cubic decimetre of it exactly precipitates 1 gramme of pure silver. It is added to the silver solution from a burette, divided into cubic centimetres, the liquid being well shaken after each addition, to cause the precipitate to settle down. The number of cubic centimetres of solution thus added determines the quantity of silver present.

As silver is reduced from many of its salts by the mere action of heat, the quantity of silver in such compounds may be readily determined by simply igniting them in a porcelain crucible. This method is applicable to nearly all salts of silver which contain organic acids. It must be observed, however, that in some cases, a certain quantity of carbon remains combined with the silver, and that some organic silver compounds containing nitrogen leave cyanide of silver when ignited.

The method of precipitating by hydrochloric acid serves to separate silver from all other metals. If lead be present in solution with silver, the liquid must be diluted with a large quantity of water before the hydrochloric acid is added; because the chloride of lead is but sparingly soluble. The separation of silver from lead may also be effected by precipitating both the metals as chlorides, and dissolving the chloride of silver in ammonia. To separate silver from mercury, the latter metal, if in the state of mercurous oxide, must first be converted into mercuric oxide by oxidation with nitric acid.

The estimation of the quantity of silver in alloys, such as coins, is usually effected either by cupellation in the manner already described (p. 332.), or by dissolving the alloy in nitric acid, and precipitating the silver with a graduated solution of chloride of sodium.*

The cupellation of silver is always attended with a certain loss, arising partly from a portion of the melted silver being absorbed by the cupel, and partly by volatilisation. The loss thus occasioned varies with the proportion of lead employed in the cupellation, with the proportion of silver in the alloy, and likewise with the heat of the furnace: hence the results obtained require a certain correction, the amount of which must be determined by special trials made upon alloys of known composition and with different proportions of lead.

SECTION III.

GOLD.

Eq. 98·33 *or* 1229·16; Au. (*Aurum.*)

Gold is found in small quantity in most countries, sometimes mixed with iron pyrites, copper pyrites, and galena, but generally native, massive, and disseminated in threads through crystalline rocks, such as quartz, or in grains among the sand of rivers, and in alluvial deposits formed by the disintegration of ancient rocks. In these deposits, some of which are of great extent, gold is occasionally found in masses of considerable size, called *nuggets*. Formerly, the principal supply of this metal was from the mines of South America, Hungary, and the Uralian mountains; but of late years, the largest quantities have been obtained from California and Australia. Native gold is sometimes pure, but is more frequently associated in various proportions with silver.

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* The process, by Guy-Lussac, for this purpose is described, with the requisite Tables, in the Parliamentary Report upon the Royal Mint, 1837, Appendix, p. 145. See also *Dr. Miller's Elements of Chemistry*, p. 1035.

Gold is separated from the substances with which it is mechanically associated, either by washing with water, whereby the earthy matters are carried away while the heavy gold particles remain behind, or by amalgamation. The small quantity of gold which occurs, generally associated with silver, in certain lead and copper ores, is extracted by liquation and cupellation, in the manner already described for silver. By these processes, gold is obtained free from all other metals except silver, and from this it may be separated by nitric acid, which dissolves the silver, but only when it forms a large proportion of the alloy. When nitric acid does not dissolve the silver, the alloy is submitted to an operation termed *quartation*, which consists in fusing it with four times its weight of silver, after which the whole of the silver may be dissolved out by nitric acid.

Pure gold may be obtained from any alloy containing it, by dissolving the alloy in a mixture of two measures of hydrochloric and one measure of nitric acid; separating the solution from insoluble chloride of silver by filtration; evaporating it over the water-bath till acid vapours cease to be exhaled; then dissolving the residue in water acidulated with hydrochloric acid; and adding protosulphate of iron, which completely precipitates the gold in the form of a brown or brownish-yellow powder, the protosulphate of iron being at the same time converted into sesquisulphate and sesquichloride:

$$6(FeO\,.\,SO_3) + Au_2Cl_3 = 2(Fe_2O_3\,.\,3SO_3) + Fe_2Cl_3 + 2Au.$$

The gold thus precipitated is quite destitute of metallic lustre, but acquires that character by burnishing.

From alloys of gold and silver, or of gold, silver, and copper, the gold may also be separated by the action of strong sulphuric acid. The alloy, after being granulated by pouring it in the melted state into water, is heated in a platinum or cast-iron vessel with 2½ times its weight of sulphuric acid of specific gravity 1·815 (66° Baumé), the heat being continued as long as sulphurous acid is evolved. The silver and copper are thereby converted into sulphates, while the gold remains unattacked. The solution is boiled for a quarter of an hour with an additional quantity of sulphuric acid of specific gravity 1·653, or 58° Baumé (obtained by concentrating the acid mother-liquors of sulphate of copper produced in the operation), and afterwards left at rest. The gold then settles down, and the liquid, after being diluted with water, is transferred to a leaden vessel and again boiled with sheets of copper immersed in it. The silver is then precipitated in the metallic state, while the copper is converted into sulphate, and dissolves. The gold deposited in the manner above described still retains a small quantity of silver, from which it is separated by treating it a second and a third time with strong sulphuric acid: it then retains only 0·005 of silver. This process is not applicable to alloys containing more than 20 per cent. of gold; richer alloys must first be fused with the requisite quantity of silver. It is applied on the large scale to the extraction of gold, chiefly from alloys which contain but little of that metal, such as native silver and old silver coins, and, as now practised, is economically available even when the amount of gold does not exceed one part in 2000.

Gold is the only metal of a yellow colour. When pure, it is more malleable than any other metal, and nearly as soft as lead. Its ductility appears to have scarcely a limit. A single grain of gold has been drawn into a wire 500 feet in length, and this metal is beaten out into leaves which have not more than 1-200,000th of an inch of thickness. The coating of gold on gilt silver wire is still thinner. Gold, when very thin, is transparent, thin gold leaf appearing green by transmitted light. The green colour passes into a ruby red when highly attenuated gold is heated: in the red gold-glass, the gold is in the metallic state (Faraday). The point of fusion of this metal is 2192°, according to Pouillet; 2518°, according to Guyton-Morveau; and 2590°, according to Daniell: it contracts considerably upon becoming solid. The density of gold varies from 19·258 to 19·367, according as it has been more or less compressed. Gold does not oxidate or tarnish in air, at the usual temperature, nor when strongly ignited. But this and the other noble metals are dissipated and partly oxidated, when a powerful electric charge is sent through them in thin leaves. It is not dissolved by nitric, hydrochloric, or sulphuric acid, or indeed by any single acid. It is acted upon by chlorine, which converts it into sesquichloride, and by acid-mixtures, such as aqua-regia, which evolve chlorine. It combines in two proportions with oxygen, forming the two oxides Au_2O and Au_2O_3, which show but little tendency to combine with acids. Some chemists, however, double the atomic weight of gold, and regard these oxides as protoxide, AuO, and teroxide, AuO_3, respectively.

Oxide of gold, Aurous oxide, Au_2O, 204·66 or 2558·25.—This oxide is obtained as a green powder by decomposing the corresponding chloride of gold with a cold solution of potash. It is partly dissolved by the alkali, and soon begins to undergo decomposition, being resolved into the higher oxide and metallic gold. The latter forms upon the sides of the vessel a thin film, which is green by transmitted light, like gold leaf.

Chloride of gold, Aurous chloride, Au_2Cl, is obtained by evaporating a solution of the sesquichloride to dryness, and heating the powder thus obtained in a sand-bath, retaining it at about the temperature of melting tin, and constantly stirring it, so long as chlorine is evolved. It is a white, saline mass, having a tinge of yellow, and quite insoluble in water. In the dry state it is permanent, but in contact with water it gradually undergoes decomposition, and is converted into gold and the sesquichloride. This change takes place almost instantaneously at the boiling temperature.

Aurous iodide, Au_2I, is formed by the action of hydriodic acid on auric oxide, water being formed and two-thirds of the iodine set free:

$$Au_2O_3 + 3HI = Au_2I + 3HO + 2I;$$

also by adding iodide of potassium in proper proportion, and in successive small quantities, to an aqueous solution of auric chloride:

$$Au_2Cl_3 + 3KI = Au_2I + 3KCl + 2I.$$

It is a lemon-yellow, crystalline powder, insoluble in cold water, and very sparingly soluble in boiling water.

Aurous sulphide is formed when hydrosulphuric acid gas is passed into a boiling solution of the sesquichloride of gold. It is dark-brown, almost black. Aurous sulphide combines with the protosulphides of potassium and sodium, forming double salts containing 1 eq. of aurous sulphide with 1 eq. of the alkaline sulphide. The sodium-salt is obtained by fusing together 2 eq. protosulphide of sodium, 1 eq. gold, and 6 eq. sulphur; digesting the fused mass in water; filtering the yellow solution in an atmosphere of nitrogen; and concentrating in vacuo over sulphuric acid. Yellow crystals are then obtained, having the form of oblique hexagonal prisms with trilateral or quadrilateral summits, and containing $NaS . Au^2S + 8Aq$. They are soluble in water and alcohol. The potassium-salt, which is obtained in a similar manner, forms indistinct crystals (Col. Yorke).*

Sesquioxide of gold, Auric oxide, Au_2O_3, 220·66 *or* 2758·25. —This oxide has many of the properties of an acid. It is obtained by digesting magnesia in a solution of sesquichloride of gold, when an insoluble compound of auric oxide and magnesia is formed, which is collected upon a filter and well washed. The compound is afterwards digested in nitric acid, which dissolves the magnesia, with traces of auric oxide, but leaves the greater part of the latter undissolved. It is left in the state of a reddish-yellow hydrate, which when dried in air becomes chestnut-brown. When precipitated by an alkali, auric oxide carries down a portion of the latter, of which it may be deprived by nitric acid. Dried at 212°, it abandons its water, becomes black, and is in part reduced. When exposed to light, particularly to the direct rays of the sun, its reduction is very rapid. It is decomposed by an incipient red heat. Hydrochloric acid is the only acid which dissolves and retains this oxide, and then sesquichloride of gold is formed. It is dissolved by concentrated nitric and sulphuric acid, but precipitated from these solutions by water. The affinity of this oxide for alkaline oxides, on the contrary, is so great that, when boiled in a solution of chloride of potassium, it is dissolved, the liquid becoming alkaline, and *aurate of potash*, or a compound of auric oxide and potash, being formed. The compounds of auric oxide with the alkalies and alkaline oxides are nearly colourless, and are not decomposed by water. They appear to be of two different degrees of saturation, aurates which are soluble, and superaurates which are insoluble. The only one of these compounds which has been studied in some degree is the aurate of ammonia, or *fulminating gold* as it is named, from its violently explosive character.

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* Chem. Soc. Qu. J. i. 236.

Aurate of ammonia.—When the solution of gold is precipitated by a small quantity of ammonia, a powder of a deep yellow colour is obtained, which is a compound of aurate of ammonia with a portion of sesquichloride of gold. This compound explodes by heat, but the detonation is not strong. But when the solution of gold is treated with an excess of ammonia, and the precipitate well washed by ebullition in a solution of ammonia, or better in water containing potash, the fulminating gold has a yellowish brown colour with a tinge of purple. When dry, it explodes very easily with a loud report, accompanied by a feeble flame. It may be exploded by a heat a little above the boiling point of water, or by the blow of a hammer. Its composition has not been exactly determined; but if the ammonia is present in double the proportion that would contain the hydrogen necessary to burn the oxygen of the auric oxide, which Berzelius considers probable, its constituents may be $Au_2O_3 . 2NH_3 + HO$. The affinity of auric oxide for ammonia is so great, that it takes that alkali from all acids. Thus, when auric oxide is digested in sulphate of ammonia, fulminating gold is formed, and the liquid becomes acid.

Aurate of potash, $KO . Au_2O_3 + 6HO$.—Obtained in the crystalline state by evaporating a solution of sesquioxide of gold in a slight excess of pure potash, first over the open fire and afterwards in vacuo: the crystals may be freed from adhering potash by recrystallisation from water, then drained on unglazed porcelain and dried in vacuo. Aurate of potash is very soluble in water, and forms a yellowish strongly alkaline solution, which is decomposed by nearly all organic bodies, the gold being precipitated in the metallic state: it is also decomposed by heat. With most metallic salts it forms precipitates of aurates, which are insoluble in water, but soluble in excess of the precipitant; thus, chloride of calcium forms a precipitate of aurate of lime, soluble in excess of chloride of calcium. The solution of aurate of potash may be used as a bath for electro-gilding.

Aurosulphite of potash, $KO . Au_2O_3 + 4(KO . 2SO_2) + 5HO$; or $5KO\left\{\begin{matrix}Au_2O_3\\8SO_2\end{matrix}\right. + 5HO$. — Deposited in beautiful yellow needles when sulphite of potash is added drop by drop to an alkaline solution of aurate of potash. It is nearly insoluble in alkaline solutions, but dissolves with decomposition in pure water, especially if hot, giving off sulphurous acid and depositing metallic gold. Acids decompose it in a similar manner. After drying in vacuo, it may be preserved for two or three months, in well-closed bottles, but ultimately decomposes, giving off sulphurous acid and leaving metallic gold and sulphate of potash. The same decomposition takes place more quickly when the salt is heated (Fremy).*

Purple of Cassius.—When protochloride of tin is added to a dilute solution of gold, a purple-coloured powder falls, which has received that name. It is obtained of a finer tint when protochloride of tin is added to a solution of the sesquichloride of iron, till the colour of the liquid takes a shade of green, and the liquid in that state added, drop by drop, to a solution of sesquichloride of gold free from nitric acid, and very dilute. After 24 hours, a brown powder is deposited, which is slightly transparent and purple-red by transmitted light. When dried and rubbed to powder, it is of a dull blue colour. Heated to redness, it loses a little water, but no oxygen, and retains its former appearance. If washed with ammonia on the filter while still moist, it is dissolved, and a purple liquid passes through, which rivals the hypermanganate of potash in beauty. From this liquid, the colouring matter separates very gradually, weeks elapsing before the upper strata of the liquid become colourless; but it is precipitated more rapidly when heated in a close vessel between 140° and 180°. The powder of Cassius is insoluble in solutions of potash and soda. It may also be formed by fusing together 2 parts of gold, 3½ parts of tin, and 15 parts of silver, under borax, to prevent the oxidation of the tin, and treating the alloy with nitric acid to dissolve out the silver; a purple residue is left containing the tin and gold that were employed.

The powder of Cassius is certainly, after ignition, a mixture of binoxide of tin and metallic gold, from which the gold can be dissolved out by aqua-regia, while the binoxide of tin is left; and the last mode of preparing it, favours the idea that its constitution is the same before ignition; but the solubility of the unignited powder in ammonia, and the fact that mercury does not dissolve out gold from the powder when properly prepared, appear to be conclusive against that opinion. The proportions of its constituents vary so much, that there must be more than one compound; or more likely the colouring compound combines with more than one proportion of binoxide of tin. Berzelius proposed the theory that the powder of Cassius may contain the true protoxide of gold combined with sesquioxide of tin, $AuO . Sn_2O_3$, a kind of combination containing an association of three atoms of metal, which is exemplified in black oxide of iron, spinell, gahnite, franklinite, and other minerals, and which we have repeatedly observed to be usually attended with great stability. A glance at its formula shows how readily the powder of Cassius, as thus represented, may pass into gold and binoxide of tin; $AuO . Sn_2O_3 = Au + 2SnO_2$. The existence of a purple oxide of gold, AuO, is not established; but it is probably the substance formed when a solution of gold is applied to the skin or nails, and which dyes them purple. Paper, coloured purple by a solution of gold, becomes gilt when placed in the moist state in phosphuretted hydrogen gas, which reduces the gold to the metallic state.

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* Ann. Ch. Pharm. lvi. 315.

Pelletier gives the following method of preparing a purple of Cassius of constant composition:—20 grammes of gold are dissolved in 100 grammes of aqua-regia containing 20 parts nitric to 80 parts of commercial hydrochloric acid; the solution is evaporated to dryness over the water-bath; the residue dissolved in water; the filtered solution diluted with 7 or 8 decilitres of water; and tin filings introduced into it: in a few minutes the liquid becomes brown and turbid, and deposits a purple precipitate, which merely requires to be washed and dried at a gentle heat. The purple thus prepared contains in 100 parts: 32·746 stannic acid, 14·618 protoxide of tin, 44·772 aurous oxide (Au_2O) and 7·864 water. The precipitate obtained by treating sesquichloride of gold with pure protochloride of tin is always brown. To obtain a fine purple precipitate, the chloride of gold should be treated with a mixture of protochloride and bichloride of tin. The following process gives a fine purple:—*a*. A neutral solution is prepared of 1 part of tin in hydrochloric acid; *b*. A solution of 2 parts tin in cold aqua-regia (1 part hydrochloric acid to 3 nitric), the liquid being merely heated towards the end of the process, that it may not contain any protoxide of tin; *c*. Seven parts of gold are dissolved in aqua-regia (6 hydrochloric to 1 nitric), and the solution, which is nearly neutral, diluted with 3500 parts of water. To this solution *c*, the solution *b* is first added, and then the solution *a*, drop by drop, till the proper colour is produced. If the quantity of *a* be too small, the precipitate is violet; if too large, it is brown. It must be washed quickly, so that the liquid may not act upon it too long. It weighs 6½ parts (Bouisson).*

Sesquisulphide of gold, Au_2S_3, or *Auric sulphide*, is formed when a dilute solution of gold is precipitated cold by hydrosulphuric acid. It is a flocculent matter of a strong yellow colour, which becomes deeper by drying; it loses its sulphur at a moderate heat.

Sesquichloride of gold, Perchloride of gold, Auric chloride, Au_2Cl_3, 303·16 or 3789·5. — This compound is formed when gold is dissolved in aqua-regia. The solution is yellow, and becomes paler with an excess of acid, but is of a deep red when neutral in composition. It is obtained in the last condition by evaporating the solution of gold, till the liquid is of a dark ruby colour, and begins to emit chlorine. It forms on cooling a dark red crystalline mass, which deliquesces quickly in air. But the only method of procuring auric chloride perfectly free from acid salt, is to decompose aurous chloride with water. A compound of chloride of gold and hydrochloric acid crystallises easily from an acid solution, in long needles of a pale yellow colour, which are permanent in dry air, but run into a liquid in damp air. The solution of this salt deposits gold on its surface, and on the side of the vessel turned to the light. The gold is also precipitated in the metallic state by phosphorus, by most metals, by ferrous salts, by arsenious and antimonious acids, and by many vegetable and animal substances, by vegetable acids, by oxalate of potash, &c., carbonic acid then escaping. Hydrosulphuric acid and sulphide of ammonium throw down black sulphide of gold, soluble in excess of the latter reagent. Ammonia and carbonate of ammonia produce a yellow precipitate of fulminating gold. Potash added in excess forms no precipitate, unless it contains organic matter, in which case a slight precipitate of aurous oxide is produced. Cyanide of potassium produces a yellow precipitate soluble in excess. Tincture of galls throws down metallic gold. Chloride of gold is soluble in ether and in some essential oils. It forms double salts with most other chlorides, which are almost all orange-coloured when crystallised; in efflorescing, they acquire a lemon-yellow colour, but in the anhydrous state they are of an intense red. They are obtained by evaporating the mixed solutions of the two salts.

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* J. Pharm. [2], xvi. 629.

Chloride of gold and potassium, $KCl . Au_2Cl_3 + 5HO$.— Crystallises in striated prisms with right summits, or in thin hexagonal tables which are very efflorescent; becomes anhydrous at 212°. The anhydrous salt fuses readily when heated, but loses chlorine and becomes a liquid, which is black while hot, and yellow when cold. It is then a compound of aurous chloride with chloride of potassium. *Chloride of gold and ammonium* crystallises in transparent prismatic needles, which become opaque in air; Mr. Johnston found their composition to be $NH_4Cl . Au_2Cl_3 + 2HO$. *Chloride of gold and sodium* crystallises in long four-sided prisms, and is persistent in air. Its composition is $NaCl . Au_2Cl_3 + 4HO$. Bonsdorff has prepared similar double salts with the chlorides of barium, strontium, calcium, magnesium, manganese, zinc, cadmium, cobalt, and nickel. The salt of lime contains six, and the salt of magnesia twelve equivalents of water.

Sesquibromide of gold, Au_2Br_3, is formed by dissolving gold in a mixture of nitric and hydrobromic acids. It greatly resembles the sesquichloride, and forms also an extensive series of double salts.

Auric iodide, Au_2I_3, is formed by gradually adding a neutral solution of auric chloride to a solution of iodide of potassium: the liquid then acquires a dark-green colour, and yields a dark-green precipitate of Au_2I_3, which redissolves on agitation; but after 1 eq. of the auric chloride has been added to 4 eqs. of iodide of potassium, a further addition of the gold-solution decolorizes the liquid and forms a permanent precipitate of auric iodide, because the iodide of gold and potassium at first produced is thereby decomposed. The successive actions are represented by the following equations: —

$$\text{(1.)} \qquad 4KI + Au_2Cl_3 = 3KCl + KI . Au_2I_3;$$

$$\text{(2.)} \qquad 3(KI . Au_2I_3) + Au_2Cl_3 = 3KCl + 4Au_2I_3.$$

Auric iodide is a very unstable compound; when exposed to the air at ordinary temperatures, it is gradually converted into yellow aurous iodide, and afterwards into metallic gold. It combines with hydriodic acid and with the more basic metallic iodides, forming a series of very dark-coloured salts; e. g. *iodo-aurate of potassium,* $KI . Au_2I_3$.

The oxides of gold show but little tendency to combine with oxygen-acids: the sesquioxide dissolves in strong nitric acid, but the solution is decomposed by evaporation or dilution.

Hyposulphite of aurous oxide and soda:

$$Au_2O . S_2O_2 + 3(NaO . S_2O_2) + 4HO; \text{ or } \left.\begin{matrix}Au_2O\\3NaO\end{matrix}\right\} 4S_2O_2 + 4HO.$$

This salt is prepared by mixing concentrated solutions of sesquichloride of gold and hyposulphite of soda, and precipitating with alcohol. When purified by repeated solution in water and precipitation by alcohol, it forms delicate, colourless needles. It has a sweetish taste, dissolves very easily in water, but very sparingly in alcohol. It is decomposed by heat and by nitric acid, with deposition of metallic gold. Its solution gives a blackish precipitate with hydrosulphuric acid and soluble sulphides. The presence of gold in this solution is not indicated by protosulphate of iron, protochloride of tin, or oxalic acid; and, on the other hand, sulphuric acid, hydrochloric acid, and the vegetable acids neither precipitate sulphur nor expel sulphurous acid from it. When mixed with chloride of barium, it yields a gelatinous precipitate of *Hyposulphite of aurous oxide and baryta*, containing $\left.\begin{matrix}Au_2O\\3BaO\end{matrix}\right\}4S_2O_2$. Sulphuric acid removes all the baryta from this salt, and leaves *hydrated aurous hyposulphite*, which is uncrystallisable, strongly acid, and tolerably stable at ordinary temperatures. The solution of the soda-salt is used for fixing daguerreotype pictures (Fordos and Gélis).*

A *hyposulphite of auric oxide and soda* appears also to be formed by dropping a neutral solution of chloride of gold into aqueous hyposulphite of soda (Fordos and Gélis).

Alloys of gold. — Gold unites with nearly all metals; but its most important alloys are those which it forms with silver and copper. Gold which is used for coins, watches, articles of jewellery, &c., is always alloyed with copper, to increase its hardness, pure gold being much too soft for any of these purposes. The standard for coin in the United Kingdom is 11 gold with 1 alloy; in France and the United States of America, 9 gold to 1 alloy. For articles of jewellery, gold is also frequently alloyed with silver, which gives it a lighter colour. The alloys of gold, both with silver and with copper, are more fusible than gold itself. The solder used for gold trinkets is composed of 5 parts gold and 1 part copper, or of 4 parts gold, 1 part copper, and 1 part silver.

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* Ann. Ch. Phys. [3], xiii. 394.

Amalgam of gold.—Gold unites readily with mercury, forming a white amalgam; the smallest quantity of mercurial vapour coming in contact with gold is sufficient to turn it white. Mercury is capable of dissolving a large quantity of gold without losing its fluidity, but, when quite saturated, it acquires a waxy consistence. When the liquid amalgam is strained through chamois-leather, mercury passes through together with a very small quantity of gold, and there remains a white amalgam, of pasty consistence, containing about 2 parts of gold to 1 part of mercury. By dissolving 1 part of gold in 1000 parts of mercury, pressing through chamois-leather, and treating the residue with dilute nitric acid at a moderate heat, a solid amalgam, Au_8Hg, is obtained, which crystallises in shining four-sided prisms, retains its lustre in the air, is not decomposed by boiling nitric acid, and does not melt even when heated till the mercury volatilises (T. H. Henry).*

Gilding and silvering.—The pasty amalgam of 2 parts gold and 1 part mercury is used for gilding ornamental articles of copper and bronze. The surface of the object is first thoroughly cleaned by heating it to redness, then plunging it into dilute sulphuric acid, and sometimes for an instant also into strong nitric acid; it is then *amalgamated* by washing it with a solution of nitrate of mercury, and afterwards pressed upon the pasty amalgam, a portion of which adheres to it. The mercury is then expelled by heat, and the gold-surface finally polished. Silver may be gilt by similar processes.

By substituting an amalgam of silver for the amalgam of gold, articles of copper, bronze, and brass may be *silvered* or *plated*.

Articles of copper, chiefly copper trinkets, are also gilt by immersion in a boiling solution of chloride of gold in an alkaline carbonate, after having been cleaned by processes similar to those just described.

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* Phil. Mag. [4], ix. 468.

But the process now most generally adopted is that of *electro-gilding*, which is performed by immersing the objects to be gilt in a solution of 10 parts of cyanide of potassium and 1 part of cyanide of gold in 100 parts of distilled water, and connecting them with the negative pole of a voltaic battery, while the positive pole is connected with a bar of gold also immersed in the liquid. The solution is then decomposed by the current, the gold being deposited on the objects at the negative pole, while the gold connected with the positive pole dissolves and keeps the solution at a nearly uniform strength. The cyanide of potassium in the solution is sometimes replaced by ferrocyanide of potassium, and the cyanide of gold by sesquioxide of gold, chloride of gold and potassium, or sulphide of gold; but the composition above given is that which is most generally adopted. This mode of gilding may be at once applied to copper, brass, bronze, silver, or platinum. To gild iron, steel, or tin, it is necessary first to deposit a layer of copper on the surface, which is effected by immersion for a few seconds in a bath of cyanide of copper and potassium.

Electro-silvering or *electro-plating* is performed in a similar manner, with a bath composed of 1 part of cyanide of silver and 10 parts of cyanide of potassium dissolved in 100 parts of water; it is principally applied to articles made of nickel-silver.

Platinum may also be deposited in a similar manner on copper or silver; but it does not adhere very firmly.

ESTIMATION OF GOLD, AND METHODS OF SEPARATING IT FROM OTHER METALS.

Gold is always estimated in the metallic state. It is generally precipitated from its solution in aqua-regia by protosulphate of iron or oxalic acid. Protosulphate of iron precipitates the gold in the form of a fine brown powder. If the gold solution is quite neutral, it must first be acidulated with hydrochloric acid, otherwise the precipitated gold will be contaminated with sesquioxide of iron formed by the action of the air on the solution of the protosulphate. If the gold solution contains much free nitric acid, there is a risk of some of the precipitated gold being redissolved by the aqua-regia present. To prevent this, the excess of nitric acid must be destroyed by adding hydrochloric acid, and boiling before the iron solution is added. Oxalic acid reduces gold slowly but completely; the gold solution must be digested with it for 24 or 48 hours.

These methods of precipitation serve to separate gold from most other metals. In such cases, oxalic acid is mostly to be preferred as the precipitating agent, because, when the quantities of the other metals are also to be determined, the presence of a large amount of iron in solution is very inconvenient.

The separation of gold in alloys may generally be effected by dissolving out the baser metals with nitric, or sometimes with hydrochloric or sulphuric acid. When, however, the proportion of gold is considerable, it may happen that the alloy is but very slowly attacked by nitric acid, especially if the other metal be silver or lead. In such a case, it is best to treat the alloy with aqua-regia, and precipitate the gold with oxalic acid. Or, again, the alloy may be fused with a known weight of lead or silver, as in the method of quartation (p. 349.), and thereby rendered decomposable by nitric acid.

The analysis or *assay* of an alloy of gold and copper is usually made by cupellation with lead. The weight of the button remaining on the cupel gives directly the amount of gold in the alloy after certain corrections similar to those required in the case of silver (p. 348.). Alloys containing both silver and copper are cupelled with lead and a quantity of silver sufficient to bring the proportion of gold and silver in the alloy to 1 part gold and 3 parts silver. The button obtained by cupellation then consists of an alloy of gold and silver, from which the silver may be dissolved out by nitric acid.

Small ornamental articles, which would be destroyed if submitted to any of the preceding processes, are approximately assayed by rubbing them on a peculiar kind of black stone, called the *touchstone,* so as to leave a streak of metal, the appearance of which may be compared with that of similar streaks produced from alloys of known composition. A further comparison is obtained by examining the appearance which the streaks present when treated with acids. This method is also sometimes used in the assaying of coins, to afford an indication of the quantity of silver required in the cupellation. The touchstone, which is a peculiar kind of bituminous quartz, was originally obtained from Lydia; but stones of similar quality are now found in Bohemia, Saxony, and Silesia.

ORDER IX.

METALS IN NATIVE PLATINUM.

SECTION I.

PLATINUM.

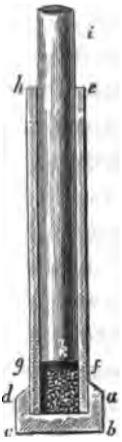
Eq. 98·68 *or* 1233·5; Pt.

THIS metal was discovered in the auriferous sand of certain rivers in America. Its name is a diminutive of *plata,* silver, and was applied to it on account of its whiteness. It occurs in the form of rounded or flattened grains of a metallic lustre. It has been found in Brazil, Colombia, Mexico, St. Domingo, and on the eastern declivity of the Ural chain; in small quantity also in certain copper-ores from the Alps; it is everywhere associated with the debris of a rock, easily recognised as belonging to one of the earliest volcanic formations.

The grains of native platinum contain from 75 to 87 per cent. of that metal, a quantity of iron generally sufficient to render them magnetic, from ½ to 1 per cent. of palladium, but sometimes much less, with small quantities of copper, rhodium, osmium, iridium, and ruthenium. To separate the platinum from these bodies, the ore is digested in a retort with hydrochloric acid, to which additions of nitric acid are made from time to time. When the hydrochloric acid is nearly saturated, the liquid is evaporated in the retort to a syrup, then diluted with water, and drawn off from the insoluble residue. If the mineral is not completely decomposed, more aqua-regia is added and the distillation continued. A portion always remains, undissolved, consisting of grains of a compound of osmium and iridium, and little brilliant plates of the same alloy, besides foreign mineral substances which may be mixed with the ore. The solution is generally deep red, and emits chlorine from the presence of perchloride of palladium; to decompose which the liquid is boiled, whereupon chlorine escapes, and the palladium is reduced to protochloride. Chloride of potassium is then added, which precipitates the platinum as a sparingly soluble double chloride of platinum and potassium, which has a yellow colour if pure, but red if it is accompanied by the double chloride of iridium and potassium. The precipitate is collected on a filter, and washed with a dilute solution of chloride of potassium. By igniting this double salt with twice its weight of carbonate of potash to the point of fusion, the platinum is reduced to the metallic state, while a portion of the iridium remains as peroxide. The soluble potash-salts are then removed by washing with hot water, and the platinum is dissolved by aqua-regia, in which the peroxide of iridium remains untouched. To complete the separation of the iridium, the precipitation by chloride of potassium and ignition with carbonate of potash may require to be repeated several times. The platinum-solution thus freed from iridium is mixed with sal-ammoniac, which throws down a yellow precipitate of the double chloride of platinum and ammonium. From this precipitate, when heated to redness, chlorine and sal-ammoniac are given off, and the platinum remains in the form of a loosely coherent mass, called *spongy platinum*. When it is not required to have platinum absolutely pure, the solution first obtained from the ore is precipitated by sal-ammoniac, and the precipitate treated in the manner just described: much of the platinum of commerce is obtained in that way. The small trace of iridium which is left in commercial platinum greatly increases its hardness and tenacity.

Platinum is too refractory to be fused in coal furnaces: but at a high temperature its particles cohere like those of iron,

Fig. 19.



and it may, like that metal, be welded, and thereby rendered malleable. For this purpose, the spongy platinum obtained by igniting the double chloride of platinum and ammonium, is introduced into a brass cylinder *e f g h* (*Fig.* 20), the lower part of which fits into a steel socket *a b c d*. The cylinder being half filled with spongy platinum, a steel piston *i k*, which fits it exactly, is introduced, and driven down by blows of a hammer, gently at first, but afterwards with greater force. The spongy platinum is thereby much reduced in bulk, and after a while is converted into a coherent disc of metal. This disc is heated to whiteness in a muffle, and afterwards hammered on a steel anvil. By repeating these operations several times, the platinum is rendered perfectly malleable and ductile, and may be rolled into sheets. Platinum in this state is the densest body at present known; its specific gravity was fixed by Dr. Wollaston at 21·53. This metal may be fused by the oxyhydrogen blow-pipe, or even made to boil, and be dissipated with scintillations. It is not acted upon by any single acid, not even by concentrated and boiling sulphuric acid. Its resistance to the action of acids, conjoined with its difficult fusibility, renders platinum invaluable for chemical experiments, and for some purposes in the chemical arts, particularly for the concentration of oil of vitriol.

The remarkable influence of a clean surface of platinum in determining the combustion of oxygen and hydrogen, has already been considered. This property platinum shares with osmium, iridium, palladium, and rhodium. It is exhibited in the greatest degree by the highly divided metal, such as platinum-sponge, the condition in which the metal is left on igniting the double chloride of platinum and ammonium. Platinum precipitated from solution by zinc, causes the combustion of alcohol vapour. The *black powder of platinum*, commonly called *platinum-black*, is the form in which that metal is most active. This is prepared by dissolving the protochloride of platinum in a hot and concentrated solution of potash, and pouring alcohol into it while still hot, by small quantities at a time; violent effervescence then occurs from the escape of carbonic acid gas, by which the contents of the vessel, unless capacious, may be thrown out. The liquor is decanted from the black powder which appears, and the latter boiled successively with alcohol, hydrochloric acid, and potash, and finally four or five times with water, to divest it of all foreign matters. Platinum-black may also be obtained by decomposing a hot solution of sulphate of platinum with alcohol; and by boiling a solution of the bichloride with carbonate of soda and sugar; chloride of sodium is then formed, water and carbonic acid are produced by oxidation of the sugar, and the platinum is precipitated in the finely-divided state. The powder, when dried, resembles lamp-black, and soils the fingers, but still it is only metallic platinum extremely divided, and may be heated to full redness without any change of appearance or properties. It loses these properties, however, by the effect of a white heat, and assumes a metallic aspect. Platinum-black, like wood charcoal, absorbs and condenses gases in its pores, with evolution of heat, a property which must assist its action on oxygen and hydrogen, although not essential to that action. When moistened with alcohol, it determines the oxidation of that substance in air, and the formation of acetic acid; and, in a similar manner, it converts wood-spirit into formic acid.

Platinum is insoluble in all acids except aqua-regia. It may be oxidated in the dry way by fusing it with hydrate of potash or nitre. Palladium, osmium, and iridium resemble platinum in their chemical relations, the corresponding compounds of these four metals being isomorphous; platinum and iridium have also the same atomic weight. Of platinum, only two degrees of oxidation are known with certainty, the protoxide, PtO, and binoxide, PtO_2.

Protoxide of platinum, Platinous oxide, PtO, 106·68 *or* 1333·5. — This oxide is obtained by digesting the corresponding chloride of platinum with potash, as a black powder, which is a hydrate. It is dissolved by an excess of the alkali, and forms a green solution, which may become black like ink with a large quantity of oxide. Protoxide of platinum forms the platinous class of salts, which have a greenish, or, sometimes red colour, and are distinguished from the platinic salts by not being precipitated by sal-ammoniac. With *hydrosulphuric acid* and *hydrosulphate of ammonia,* they form a black precipitate, soluble in a large excess of the latter; with *mercurous nitrate,* a black precipitate; with *potash,* no precipitate; with *carbonate of potash or soda,* a brownish precipitate. *Ammonia* added to the hydrochloric acid solution throws down a green crystalline precipitate of ammonio-platinous chloride; carbonate of ammonia forms no precipitate.

Protosulphide of platinum, PtS, is thrown down as a black precipitate, when the protochloride of platinum is decomposed by hydrosulphuric acid. It may be washed and dried without decomposition.

Protochloride of platinum, Platinous chloride, PtCl, is obtained by evaporating a solution of the bichloride of platinum to dryness; triturating the dry mass; and heating it in a porcelain capsule by a sand-bath at the melting point of tin, taking care to stir it at the same time, so long as chlorine is evolved. It remains as a greenish grey powder, quite insoluble in water, and repelling that liquid so as not to be moistened by it. This chloride is not decomposed by sulphuric or nitric acid, but is partially soluble in boiling and concentrated hydrochloric acid. From the last solution, alkalies throw down a black precipitate of protoxide. When the calcination of the bichloride of platinum, at 420° or 460°, is interrupted before the whole of the chlorine is expelled, the residue yields to water a compound of a brown colour, so deep, that the liquid becomes opaque. This, Professor Magnus believes to be a combination of the two chlorides of platinum. A double *protochloride of platinum and potassium*, or *chloroplatinite of potassium*, $PtCl . KCl$, is obtained on adding chloride of potassium to the solution of platinous chloride in hydrochloric acid, and evaporating the liquid. The salt crystallises in red four-sided prisms, the form of which is the same as that of a corresponding salt of palladium; it is anhydrous. A protochloride of platinum and sodium also exists, but does not crystallise easily.

Corresponding *platinous iodides* and *cyanides* have been formed. The cyanide forms a numerous class of double salts, called *platinocyanides,* whose general formula is $MCy.PtCy$. The potassium salt is obtained by heating spongy platinum with ferrocyanide of potassium; exhausting the mass with hot water and crystallising; or by treating platinous chloride with aqueous cyanide of potassium. The salt crystallises in needles and rhombic prisms, pale yellow by transmitted light, yellow or blue by reflected light, according to the direction in which they are viewed. From the solution of this salt, the platino-cyanides of zinc, lead, copper, mercury, and silver, which are insoluble, are obtained by precipitation. The sodium, barium, strontium, and calcium-salts, which are soluble, are obtained by treating the copper-salt with caustic soda, baryta, &c.; and the magnesium and aluminum-salts, by precipitating the barium-salt with sulphate of magnesia or alumina. The ammonium-salt is prepared like the potassium-salt. Platinous oxide has also been united with several acids, particularly sulphuric, nitric, oxalic, and acetic acids; but none of these salts have been crystallised, except the oxalate.

Bioxide of platinum, Peroxide of platinum, Platinic oxide, PtO_2, 114·68 *or* 1433·5.—By precipitating sulphate of platinum with nitrate of baryta, nitrate of platinum is obtained.

One half of its oxide may be precipitated by soda, from the last salt, but when a larger quantity of alkali is added, a subsalt is thrown down. The precipitated oxide is hydrated, very bulky, and exactly resembles sesquioxide of iron precipitated by ammonia. When heated, it first loses its water, and becomes black, then its oxygen, and leaves metallic platinum. Bioxide of platinum combines with acids, and forms a class of salts, which are either yellow or reddish-brown. From the solutions of these salts, the platinum is precipitated in the metallic state by *phosphorus* and by most *metals*. *Hydrosulphuric acid* and *sulphide of ammonium* form a black precipitate soluble in a large excess of the latter. In a solution of platinic chloride, *potash* or *ammonia* forms a yellow crystalline precipitate of chloroplatinate of potassium or ammonium; so likewise do the *chlorides of potassium* or *ammonium*; sodium-salts form no precipitate. In the solution of platinic nitrate or sulphate, *potash* or *ammonia* forms a yellow-brown precipitate; *chloride of potassium* or *ammonium* produces, after some time, a slight yellow precipitate of the double chloride. Platinic oxide has also a decided affinity for bases, and forms insoluble compounds with the alkalies, earths, and many metallic oxides. It forms also, like sesquioxide of gold, a fulminating ammoniacal compound, discovered by Mr. E. Davy.

Bisulphide of platinum, PtS_2, is formed by adding a solution of bichloride of platinum, drop by drop, to a solution of sulphide of potassium. It is dark brown and becomes black by desiccation. When dried in open air, a portion of its sulphur is converted into sulphuric acid, by absorption of oxygen, and the mass becomes strongly acid.

Bichloride of platinum, $PtCl_2$, 2121 *or* 169·68, is obtained by concentrating the solution of platinum in aqua-regia, as a red saline mass, which becomes brown when deprived of its water of crystallisation by heat. The solution of this salt when pure has an intense and unmixed yellow colour, the red colour which it usually exhibits being due to iridium or to protochloride of platinum. Bichloride of platinum is soluble in alcohol, and the solution is used to separate potash and ammonia in analysis.

Chloride of platinum and potassium, Chloroplatinate of potassium, $KCl . PtCl_2$, is the salt which falls on mixing chloride of platinum with chloride of potassium or any other salt of potash. The crystalline grains of which it is composed are regular octohedrons. This salt is soluble to a certain extent in water, but is wholly insoluble in alcohol. It is anhydrous. A very intense red-heat is required for its complete decomposition. *Chloroplatinate of sodium,* $NaCl . PtCl_2 + 6HO$, crystallises in beautiful transparent prisms of a bright yellow colour. It is soluble in alcohol as well as in water. When a solution of this salt in alcohol is distilled till only one-fourth of the liquid remains, the solution yields by evaporation a salt containing the elements of ether, and belonging to a class of compounds discovered by Professor Zeise, and known as the etherised salts of Zeise.

Chloroplatinate of ammonium resembles the double salt of potassium. When ignited, it leaves metallic platinum in the spongy state. Bonsdorff has formed a large class of compounds of bichloride of platinum with the alkaline, earthy, and metallic chlorides, in all of which the salts are united in single equivalents. The bromides and iodides of platinum have likewise been formed, and classes of double salts derived from them. Bioxide of platinum has also been combined with acids; but none of its salts, with the exception of the oxalate, is obtained in a crystalline state.

Bicyanide of platinum, or *platinic cyanide,* does not appear to exist in the separate state; but it forms double salts with the cyanides of potassium and ammonium; it likewise combines with chloride of potassium, forming the compound $KCl . PtCy_2$.

The *sulphocyanides of platinum,* $PtCyS_2$, and $Pt . (CyS_2)_2$, likewise form two series of double salts, viz. the *platino-bisulphocyanides* or *sulphocyanoplatinites* = $MPt(CyS_2)_2$, or $MCyS_2 + PtCyS_2$, and the *platino-tersulphocyanides* or *sulphocyanoplatinates* = $MPt(CyS_2)_3$, or $MCyS_2 + Pt(CyS_2)_2$. The potassium salts are formed by the action of sulphocyanide of potassium on protochloride and bichloride of platinum respectively. All these salts are strongly coloured, exhibiting all shades of colour from light yellow to deep red. They are quickly decomposed by heat (G. B. Buckton).*

AMMONIACAL PLATINUM SALTS.

The oxides, chlorides, sulphates, &c., of platinum are capable of taking up the elements of 1 or 2 equivalents of ammonia, giving rise to four series of compounds, whose composition may be represented by the following general formulæ, in which the symbols R, R′ denote acid elements:

1. Ammonio-platinous compounds, or protosalts of platammonium,

$$NH_3PtR = \overbrace{NH_3Pt}.R.$$

2. Biammonio-platinous compounds, or protosalts of ammoplatammonium,

$$N_2H_6PtR = \overbrace{NH_2(NH_4)Pt}.R.$$

3. Ammonio-platinic compounds, or bisalts of platammonium,

$$NH_3Pt\left\{\begin{array}{l} R_2 \\ \text{or } RR' \end{array}\right. = \overbrace{NH_3Pt}.\left\{\begin{array}{l} R_2 \\ \text{or } RR'. \end{array}\right.$$

4. Biammonio-platinic compounds, or bisalts of ammoplatammonium,

$$N_2H_6Pt\left\{\begin{array}{l} R_2 \\ \text{or } RR' \end{array}\right. = \overbrace{NH_2(NH_4)Pt}.\left\{\begin{array}{l} R_2 \\ \text{or } RR'. \end{array}\right.$$

The third and fourth classes of these compounds may also be regarded as protosalts of compound ammoniums, in which

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* Chem. Soc. Qu. J. vii. 22.

1 eq. of hydrogen is replaced by PtO or PtCl; for example, the bichloride $NH_3PtCl_2 = N\overbrace{H_3(PtCl)}.Cl$; the chloronitrate $N_2H_6PtClNO_6 = N\overbrace{H_2(NH_4)PtCl}.NO_6$.

1. *Ammonio-platinous compounds, or Protosalts of Platammonium.* — These compounds are formed by the action of heat on those of the following series, half the ammonia of the latter being then given off. They are for the most part insoluble in water, but dissolve in ammonia, reproducing the biammoniacal platinous compounds; they detonate when heated.

Oxide, $NH_3PtO = N\overbrace{H_3Pt}.O$.—Obtained by heating the hydrated oxide of biammo-platammonium to 230°. It is a greyish mass which, when heated to 392° in a close vessel, gives off water, ammonia, and nitrogen, and leaves metallic platinum. Probably the compound, Pt_3N, is first produced and is afterwards resolved into nitrogen and platinum:

$$3NH_3PtO = Pt_3N + 3HO + 2NH_3.$$

The oxide, heated to 392° in contact with the air, becomes incandescent, and burns vividly, leaving a residue of platinum.

Chloride, $NH_3PtCl = N\overbrace{H_3Pt}.Cl$. — Of this compound three isomeric modifications exist: *α. Yellow,* obtained by adding hydrochloric acid, or a soluble chloride, to a solution of nitrate or sulphate of platammonium. Or, by boiling the green modification, *γ*, with nitrate or sulphate of ammonia, whereupon it dissolves and forms a solution which, on cooling, deposits the yellow salt. Or, by neutralising a solution of platinous chloride in hydrochloric acid with carbonate of ammonia, heating the mixture to the boiling point, and adding a quantity of ammonia equal to that already contained in the liquid, filtering from a dingy green substance, which deposits after a while, then leaving the solution to cool, and decanting the supernatant liquid as soon as the yellow salt is deposited. β. *Red.*—If, in the last mode of preparation, the carbonate of ammonia, instead of being added at once in excess, be added drop by drop to the hydrochloric acid solution of platinous chloride, the liquid on cooling deposits small garnet-coloured crystals having the form of six-sided tables. This red modification may also be obtained in other ways (Peyrone).* γ. *Green.* — This modification, usually denominated the *green salt of Magnus*, was the first discovered of the ammoniacal platinum compounds. It is obtained by gradually adding an acid solution of platinous chloride to caustic ammonia, or by passing sulphurous acid gas into a boiling solution of bichloride of platinum till it is completely converted into protochloride (and therefore no longer gives a precipitate with sal-ammoniac), and neutralising the solution with ammonia ; the compound is then deposited in green needles. The same modification of the salt may also be obtained by adding an acid solution of platinous chloride to a solution of biammonio-platinous chloride, N_2H_6PtCl. Hence it would appear that the true formula of this green salt is $(NH_3PtCl)_2 = PtCl + \overbrace{NH_2(NH_4)Pt}.Cl$, that of the yellow or red modification being simply NH_3PtCl. Either modification of the salt, when heated to 572°, gives off nitrogen, hydrochloric acid, and sal-ammoniac, and leaves a residue of platinum.

A red crystalline compound of chloride of platammonium with chloride of ammonium, viz. $NH_3PtCl + NH_4Cl$, is formed when a solution of chloride of ammo-platammonium, containing a large quantity of sal-ammoniac, is evaporated to the crystallising point. Thus, when a solution of platinous chloride in hydrochloric acid is precipitated by ammonia, and the green salt of Magnus thereby formed is heated, while still in the liquid, with excess of ammonia, to convert it into chloride of ammo-platammonium, the red compound separates at a certain degree of concentration, together with the chloride of ammo-platammonium (Grimm).*

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* Vide Translation of Gmelin's Handbook, vi. 303.

Iodide, NH_3PtI.—Yellow powder, obtained by boiling the aqueous solution of the compound N_2H_6PtI. It dissolves in ammonia, and is thereby reconverted into the latter compound.

Cyanide, NH_3PtCy.—Obtained by adding hydrocyanic acid to a solution of biammonio-platinous oxide, cyanide of ammonium being formed at the same time (Reiset):

$$N_2H_6PtO + 2HCy = NH_3PtCy + NH_4Cy + HO.$$

Also, by digesting ammonio-platinous chloride with cyanide of silver. It crystallises in fine regular needles of a pale yellow colour, soluble with tolerable facility in water and ammonia. An isomeric modification of this compound, $(NH_3PtCy)_2 = N_2H_6PtCy + PtCy$, is formed by passing cyanogen gas into a moderately concentrated solution of biammonio-platinous oxide; the cyanogen then decomposes the water, forming hydrocyanic and cyanic acids, and the hydrocyanic acid acts upon the biammonio-platinous oxide, forming the compound $(NH_3PtCy)_2$, together with ammonia and water:

$$2(N_2H_6PtO) + 2HCy = (NH_3PtCy)_2 + 2NH_3 + 2HO.$$

The compound, $(NH_3PtCy)_2$, crystallises out and may be purified by recrystallisation from water. It is also obtained by mixing a solution of biammonio-platinous chloride with cyanide of potassium. It forms crystals which, under the microscope, appear like six-sided tables arranged in stellate groups; it dissolves without decomposition in potash, hydrochloric acid, and dilute sulphuric acid, but is decomposed by strong sulphuric and by nitric acids (Buckton).†

The sulphate, $NH_3Pt.SO_4.HO$, and the *nitrate*, $NH_3Pt.NO_6$, are obtained by boiling the iodide with sulphate and nitrate of silver; they are crystalline, and have a strong acid reaction. The sulphate retains one atom of water, which cannot be removed without decomposing the salt.

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* Ann. Ch. Pharm. xcix. 95.

† Chem. Soc. Qu. J., iv. 34.

2. *Biammonio-platinous compounds, or Protosalts of Ammoplatammonium.*—*Oxide,* $N_2H_6PtO \,.\, HO = N\overbrace{H_2(NH_4)Pt}\,.\,O + HO$.—Obtained by decomposing the solution of the sulphate with an equivalent quantity of baryta-water, and evaporating the filtrate in vacuo; a crystalline mass is then left, containing $N_2H_6PtO \,.\, HO$. The oxide is not known in the anhydrous state. The hydrate is strongly alkaline and caustic, like potash, absorbs carbonic acid rapidly from the air, and precipitates oxide of silver from the solution of the nitrate. It is a strong base, neutralising acids completely, and expelling ammonia from its salts. It melts at 230°, giving off water and ammonia, and leaving the compound NH_3PtO. Its aqueous solution does not give off ammonia, even when boiled.

Chloride, $N_2H_6PtCl = N\overbrace{H_2(NH_4)Pt}\,.\,Cl$.—This compound is prepared by boiling protochloride of platinum, or the green salt of Magnus, with aqueous ammonia, till the whole is dissolved, and evaporating the liquid to the crystallising point. Or, by passing sulphurous acid gas into bichloride of platinum till the solution is completely decolorised, precipitating with carbonate of soda, dissolving the precipitate of sodio-platinous sulphite in hydrochloric acid, saturating the resulting solution of chloride of sodium and platinous chloride with ammonia, and dissolving the precipitate of N_2H_6PtCl and NH_3PtCl in boiling hydrochloric acid. The filtered liquid on cooling deposits NH_3PtCl, while the biammoniacal compound remains in solution and may be obtained by evaporation, mixed however, with sal-ammoniac. It separates in bulky crystals of a faint yellow colour, containing 1 eq. water, which is completely given off at 230°. At 482° it gives off ammonia, and leaves NH_3PtCl. The anhydrous compound rapidly absorbs water from the air. The hydrate does not give off ammonia when treated with caustic alkalies in the cold, and is but very slowly decomposed by them, even with the aid of heat.

Chloride of ammo-platammonium forms two compounds with bichloride of platinum. The first, whose formula is $2(\overbrace{NH_2(NH_4)Pt}.Cl) + PtCl_2$, is obtained as an olive-green precipitate on adding bichloride of platinum to a solution of $\overbrace{NH_2(NH_4)Pt}.Cl$; the second, $\overbrace{NH_2(NH_4)Pt}.Cl + PtCl_2$, by treating the preceding with excess of bichloride of platinum.

The *bromide* and *iodide* of this series are obtained by treating the solution of the sulphate with bromide or iodide of barium: they crystallise in cubes.

The *sulphate*, $\overbrace{NH_2(NH_4)Pt}.SO_4$, and the *nitrate*, $NH_2(NH_4)Pt.NO_6$, are obtained by decomposing the chloride with sulphate or nitrate of silver; they are neutral, and crystallise easily.

Carbonates.—The hydrated oxide absorbs carbonic acid rapidly from the air, forming first, a neutral carbonate, $\overbrace{NH_2(NH_4)Pt}.CO_3 + HO$, and afterwards an acid salt, $\overbrace{NH_2(NH_4)Pt}.CO_3 + CO_3H$.

3. *Ammonio-platinic compounds*; or, *Bi-salts of platammonium.*—The *oxide*, $NH_3PtO_2 = \overbrace{NH_3Pt}.O_2$, may also be regarded as *oxide of oxyplatammonium*, $\overbrace{NH_3(PtO)}.O$. It is obtained by adding ammonium to a boiling solution of ammonio-platinic nitrate; it is then precipitated in the form of a heavy, yellowish, crystalline powder, composed of small, shining, rhomboidal prisms; it is nearly insoluble in boiling water, and resists the action of boiling potash. Heated in a close vessel, it gives off water and ammonia, and leaves metallic platinum. It dissolves readily in dilute acids, even in acetic

acid, and forms a large number of crystallisable salts, both neutral and acid, having a yellow colour, and sparingly soluble in water (Gerhardt).* Another compound of platinic oxide with ammonia, called *fulminating platinum*, whose composition has not been exactly ascertained, is produced by decomposing chloroplatinate of ammonium with aqueous potash. It is a straw-coloured powder which detonates slightly when suddenly heated, but strongly when exposed to a gradually increasing heat.

Chloride, $NH_3PtCl_2 = \overparen{NH_3Pt}\,.\,Cl_2 = \overparen{NH_3\,(PtCl)}\,.\,Cl$. — Obtained by passing chlorine gas into boiling water in which the compound NH_3PtCl (the yellow modification) is suspended. This compound is insoluble in cold water, and very slightly soluble in boiling water, or in water containing hydrochloric acid. It dissolves in ammonia at a boiling heat, and the solution, on cooling, deposits a yellow precipitate, consisting of biammoniacal platinic chloride. The compound $NH_3Pt\,.\,Cl_2$ dissolves in boiling potash without evolving ammonia. An isomeric compound,

$$(NH_3PtCl_2)_2 = N_2H_6PtCl_2 + PtCl_2,$$

is obtained by passing chlorine into water in which Magnus's green salt is suspended. A red crystalline powder is at first precipitated, consisting of $N_2H_6PtCl + PtCl_2$; but on continuing the passage of the chlorine, this precipitate redissolves, and the solution yields, by evaporation, the crystalline compound $(NH_3PtCl_2)_2$.

The *sulphate*, $NH_3Pt\,.\,(SO_4)_2$, is obtained by dissolving the oxide in dilute sulphuric acid, and evaporating. It is a yellow powder, having an acid taste, and is soluble in boiling water.

Nitrates. — A *mononitrate*, $NH_3PtO_2\,.\,NO_5 + 3HO$, or *oxynitrate*, $\overparen{NH_3Pt}\,.\left\{\begin{matrix}NO_6\\ O\end{matrix}\right. + 3HO$, or *nitrate of oxyplat-*

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* Comptes Rendus des Travaux de Chimie, 1849, p. 273.

ammonium, $\overbrace{NH_3(PtO)}.NO_6 + 3HO$, is obtained by boiling the chloride NH_3PtCl_2 for several hours with a dilute solution of nitrate of silver. It is a yellow, crystalline powder, sparingly soluble in cold, more soluble in boiling water. The *binitrate*, $\overbrace{NH_3Pt}.2NO_6 + 2HO$, is obtained by dissolving the mononitrate in nitric acid: it is yellowish, insoluble in cold water, soluble in hot nitric acid.

The *oxalate*, $NH_3PtO_2.C_2O_3 + 2HO$, or $NH_3Pt\left\{\begin{matrix}C_2O_4\\O\end{matrix}\right. + 2HO$, or $\overbrace{NH_3(PtO)}.C_2O_4 + 2HO$, is formed by decomposing the nitrate with oxalate of ammonia. It is a light yellow precipitate, soluble in boiling water, and detonating when heated.

4. *Biammonio-platinic compounds*, or *Bi-salts of ammoplatammonium.* — The oxide of this series has not yet been isolated.

Chloride. — $N_2H_6PtCl_2 = N\overbrace{H_2(NH_4)Pt}.Cl_2 = \overbrace{NH_2(NH_4)(PtCl)}.Cl$. — Obtained by passing chlorine gas into a solution of biammonio-platinous chloride, N_2H_6PtCl; by dissolving ammonio-platinic chloride, NH_3PtCl_2, in ammonia, and expelling the excess of ammonia by evaporation; or by precipitating a solution of one of the nitrates,

$$N_2H_6PtO_2.NO_5, \text{ or } N_2H_6PtClO.NO_5,$$

with hydrochloric acid. It is white, and dissolves in small quantity in boiling water, from which solution it is deposited in the form of transparent, regular octohedrons, having a faint yellow tint. When a solution of this salt is treated with nitrate of silver, one half of the chlorine is very easily precipitated, but to remove even a small portion of the remainder requires a long-continued action of the silver-salt; a result easily explained if the salt be regarded as a chloride of ammo-chlorplatammonium, $\overbrace{NH_2(NH_4)(PtCl)}.Cl$ (Grimm.)* A compound having the formula N_2H_5PtCl, containing, therefore, 1 eq. Cl and 1 eq. H less than the preceding, is obtained by dissolving chloroplatinate of ammonium in ammonia, and precipitating by alcohol; but it does not crystallise, merely drying up to a pale yellow, resinous mass: hence its composition is doubtful.

Nitrates.—A mononitrate, $N_2H_6PtO_2.NO_5$, or oxynitrate of ammoplatammonium, $\overbrace{NH_2(NH_4)Pt}\left\{\begin{matrix}NO_6\\O\end{matrix}\right.$, or nitrate of ammoxyplatammonium, $\overbrace{NH_2(NH_4)(PtO)}.NO_6$, is obtained by boiling the following salt *b*, with ammonia: it is a white amorphous powder, slightly soluble in cold, more soluble in boiling water.

Sesquinitrate, $2(N_2H_6PtO_2).3NO_5$, or

$$2\left(\overbrace{NH_2(NH_4)Pt}\right).\left\{\begin{matrix}3NO_6\\O\end{matrix}\right., \text{ or } \left.\begin{matrix}\overbrace{NH_2(NH_4)(PtO)}\\\overbrace{NH_2(NH_4)(PtNO_6)}\end{matrix}\right\}2NO_6.—$$

Formed by boiling the mononitrate of ammoplatammonium with nitric acid. It is a colourless, crystalline, detonating salt, slightly soluble in cold water, more soluble in boiling water, insoluble in nitric acid (Gerhardt).

Chloronitrates.—*a.* $N_2H_6PtClO.NO_5$; or $\overbrace{NH_2(NH_4)Pt}.\left\{\begin{matrix}NO_6\\Cl\end{matrix}\right.$, or $\overbrace{NH_2(NH_4)(PtCl)}.NO_6$.—This salt was discovered by Gros. It is obtained by treating Magnus's green salt with strong nitric acid. The green compound first turns brown, and is afterwards converted into a mixture of platinum and a white powder, which is dissolved out by boiling water, and crystallises on cooling in shining flattened prisms, colourless, or having a pale yellow tint. The reaction may be thus represented:—

$$2(NH_3PtCl)+HO.NO_5=N_2H_6PtCl.NO_6+Pt+HCl.$$

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* Ann. Ch. Pharm. xcix. 77.

This compound dissolves readily in water, especially when heated. The chlorine and platinum contained in the solution cannot be detected by the ordinary reagents; thus, nitrate of silver and hydrosulphuric acid yield but very trifling precipitates, even after a long time.

$$b.\ 4NH_3 . Pt_2ClO_3 . 2NO_5,\ \text{or}\ \left.\begin{matrix}\overbrace{NH_2(NH_4)(PtCl)}\\ \overbrace{NH_2(NH_4)(PtCl)}\end{matrix}\right\} . 2NO_6.$$

Discovered by Raewsky. When Magnus's green salt is boiled with a large excess of nitric acid, red fumes are evolved, and the resulting solution deposits this salt in small, brilliant, needle-shaped prisms, which deflagrate when heated, giving off water and chloride of ammonium, and leaving metallic platinum. Raewsky assigns to this salt the formula $4NH_3 . Pt_2ClO_5 . 2NO_5$; but the formula above given, which is deduced from Gerhardt's analysis, and contains 2O less, is much more probable, as it accords with the constitution of the other compounds of the series. The 2 atoms of nitric acid contained in this salt may be replaced by 2 atoms of *carbonic* or *oxalic* acid, yielding sparingly soluble crystalline salts of exactly similar constitution. There is also a *phosphate* containing $4NH_3 . Pt_2ClO_3 . PO_5 . HO$, obtained by mixing the solution of the nitrate with ordinary phosphate of soda. According to Raewsky, the mother-liquor from which the preceding nitrate has crystallised, contains another nitrate whose formula is $4NH_3 . Pt_2Cl_2O_4 . 2NO_5$; but Gerhardt finds this salt to be identical with the nitrate discovered by Gros.

Chlorosulphate, $N_2H_8PtClSO_4 = NH_2\overbrace{(NH_4)(PtCl)} . SO_4$.—Obtained by treating biammonio-platinic chloride, or Gros's nitrate, with dilute sulphuric acid, or by mixing the solution of the nitrate with a strong solution of a soluble sulphate. It crystallises in slender needles, sparingly soluble in cold water, but dissolving with tolerable facility in boiling water. The sulphuric acid in the solution is not precipitated by baryta-salts. The salt is, however, decomposed by hydrochloric or nitric acid, either of which takes the place of the sulphuric acid, reproducing the chloride or nitrate (Gros).

Chloroxalate, $N_2H_6PtClO \,.\, C_2O_3 = \overbrace{NH_2(NH_4)Pt}\left\{\begin{matrix}C_2O_4\\ Cl\end{matrix}\right. = \overbrace{NH_2(NH_4)(PtCl)} \,.\, C_2O_4$.—Oxalic acid or an alkaline oxalate added to the solution of the corresponding sulphate or nitrate, throws down this salt in the form of a white granular precipitate, insoluble in water.

Oxalonitrates. — *a.* $N_2H_6PtO_2 \,.\, NO_5 \,.\, C_2O_3 =$

$$\overbrace{NH_2(NH_4)Pt}.\left\{\begin{matrix}NO_6\\ C_2O_4\end{matrix}\right. = \overbrace{NH_2(NH_4)(PtNO_6)} \,.\, C_2O_4.$$

Deposited as a white crystalline body from a solution of the following salt *b* in dilute nitric acid.

b. $2(N_2H_6PtO_2) \,.\, NO_5 \,.\, 2C_2O_3 = 2(\overbrace{NH_2(NH_4)Pt}) \,.\left\{\begin{matrix}2C_2O_4\\ NO_6\\ O\end{matrix}\right. = \left.\begin{matrix}\overbrace{NH_2(NH_4)(PtO)}\\ NH_2(NH_4)(PtNO_6)\end{matrix}\right\} 2C_2O_4$.—Obtained by adding oxalate of ammonia to a solution of the sesquinitrate; it is insoluble in water (Gerhardt).

GERHARDT'S THEORY OF THE AMMONIACAL PLATINUM COMPOUNDS.

These compounds may be regarded as salts of peculiar bases or alkalies, formed from ammonia by the substitution of one or two atoms of platinum for hydrogen; admitting, however, that platinum (like other metals) may enter into its compounds with two different equivalent weights, viz., in the platin*ous* compounds, as *Platinosum* = 98·68 = Pt, and in the platin*ic* compounds, as *Platinicum* = 49·34 = pt. This being admitted, the ammonio-platinous compounds may be regarded as salts of an alkali, called *Platosamine* = NH_2Pt, formed from ammonia by the substitution of 1 atom of platinosum for 1 atom of hydrogen; and the biammonio-platinous compounds, as salts of *Diplatosamine* = N_2H_5Pt, formed by the union of two atoms of ammonia into one, and the substitution therein of 1 Pt for 1 H: thus for the chlorides:—

NH_3PtCl = Hydrochlorate of Platosamine = $NH_2Pt . HCl$;

N_2H_6PtCl = Hydrochlorate of Diplatosamine = $N_2H_5Pt.HCl$;

and for the nitrates:—

$NH_3Pt.NO_6$ = Nitrate of Platosamine = $NH_2Pt . HNO_6$;

$N_2H_6Pt.NO_6$ = Nitrate of Diplatosamine = $N_2H_5Pt . HNO_6$.

In a similar manner, the ammonio-platinic compounds may be regarded as salts of *Platinamine* = $NHpt_2$, and the biammonio-platinic compounds as salts of *Diplatinamine* = $N_2H_4pt_2$; thus—

NH_3PtCl_2 = Bihydrochlorate of Platinamine = $NHpt_2 . 2HCl$.

$N_2H_6PtCl_2$ = Bihydrochlorate of Diplatinamine = $N_2H_4pt_2 . 2HCl$.

Diplatinamine forms three kinds of salts, viz., mono-acid, sesqui-acid, and bi-acid salts; and, moreover, exhibits a peculiar tendency to form double salts containing two acids: thus, the salts discovered by Gros may be regarded as bi-acid salts, and those discovered by Raewsky, as sesqui-acid salts of diplatinamine containing hydrochloric together with another acid; thus:—

$$\text{Mononitrate} = N_2H_6PtO_2 . NO_5 = N_2H_4pt_2 . HNO_6 + HO.$$

$$\text{Sesquinitrate} = 2(N_2H_6PtO_2) . 3NO_5 = 2N_2H_4pt_2 . 3HNO_6 + HO.$$

$$\left.\begin{matrix}\text{Chloronitrate}\\ \text{(Gros's nitrate)}\end{matrix}\right\} = N_2H_6PtClO . NO_5 = N_2H_4pt_2 . \left\{\begin{matrix}HCl\\ HNO_6\end{matrix}\right.$$

$$\left.\begin{matrix}\text{Sesquichloronitrate}\\ \text{(Raewsky's nitrate)}\end{matrix}\right\} = N_4H_{12}Pt_2ClO_3.2NO_5 = 2N_2H_4pt_2 . \left\{\begin{matrix}HCl\\ 2HNO_6\end{matrix}\right. + HO.$$

$$\text{Oxalonitrate} = N_2H_6PtO_2 . NO_5 . C_2O_3 = N_2H_4pt_2 . \left\{\begin{matrix}C_2HO_4\\ HNO_6.\end{matrix}\right.$$

$$\text{Sesqui-oxalonitrate} = 2(N_2H_6PtO_2) . NO_5 . 2C_2O_3 =$$
$$2N_2H_4pt_2 . \left\{\begin{matrix}2C_2HO_4\\ HNO_6\end{matrix}\right. + HO.$$

ESTIMATION AND SEPARATION OF PLATINUM.

For quantitative estimation, platinum is usually precipitated from its solutions in the form of chloroplatinate of ammonium. The acid solution of platinum, after sufficient concentration, is mixed with a very strong solution of sal-ammoniac, and a sufficient quantity of strong alcohol added to render the precipitation complete. The precipitate of chloroplatinate of ammonium is then washed with alcohol, to which a small quantity of sal-ammoniac has been added, and then heated to redness in a weighed porcelain crucible, whereupon it is decomposed and leaves metallic platinum. Great care must, however, be taken in the ignition to prevent loss, as the evolved vapours are very apt to carry away small particles of the salt and of the reduced metal. The best mode of avoiding this source of error is to place the precipitate in the crucible *enclosed in the filter*, and expose it for some time to a moderate heat, with the cover on the crucible, till the filter is charred, and then to a somewhat higher temperature to expel the chlorine and chloride of ammonium. The crucible is then partially opened and the carbonaceous matter of the filter burnt away in the usual manner. When these precautions are duly observed, not a particle of platinum is lost. Instead of igniting the precipitate and weighing the platinum, the precipitate is sometimes collected on a weighed filter, dried over the water-bath and weighed; but this method is less accurate, because the precipitate always contains an excess of sal-ammoniac (H. Rose).

Chloride of potassium may also be used instead of chloride of ammonium to precipitate platinum, the concentrated solution of the platinum being previously mixed with a sufficient quantity of strong alcohol to bring the per centage of alcohol in the liquid to between 60 and 70 per cent. The precipitated chloroplatinate of potassium is then washed with alcohol of

60 to 70 per cent. and decomposed by simple ignition in a porcelain crucible, if its quantity is small, or in an atmosphere of hydrogen if its quantity is larger; the chloride of potassium washed out by water; and the platinum dried, ignited, and weighed.

Potash and ammonia may also be estimated by precipitating their solutions with chloride of platinum, and treating the precipitates in the manner just described. Every 100 parts of platinum correspond to 47·83 parts of potash, and 17·25 parts of ammonia.

The same methods of precipitation serve also for the separation of platinum from most of the preceding metals. To separate platinum from *silver*, when the two metals are combined in an alloy, the best method is to heat the alloy with pure and strong sulphuric acid, diluted with about half its weight of water, till the sulphuric acid begins to escape in dense fumes. The silver is thereby converted into sulphate, and the platinum remains behind in the metallic state. The sulphate of silver is dissolved by a large quantity of hot water, the platinum washed with hot water, and again treated with sulphuric acid, to separate the last traces of silver.

SECTION II.

PALLADIUM.

Eq. 53·36 *or* 665·9; Pd.

This metal was discovered in 1803 by Dr. Wollaston. It is precipitated by cyanide of mercury from the solution of the ore of platinum, after the removal of that metal by sal-ammoniac, and is gradually deposited as a yellowish white flocculent powder, which is cyanide of palladium, and yields the metal when calcined. Palladium likewise occurs, associated with a larger quantity of gold and a small quantity of silver, in a peculiar gold-ore from Brazil, called *oropudre*. This mineral, which contains 10 per cent. of palladium, and is the chief source of that metal, is dissolved in aqua-regia, the acid solution saturated with potash, and the palladium precipitated by cyanide of mercury.

In external characters, palladium closely resembles platinum. It is nearly as infusible, but can more easily be welded. The density of the fused metal is 11·3; after being laminated, 11·8. At a certain temperature, the surface of palladium tarnishes and becomes blue from oxidation, but at a stronger heat the oxide is reduced. Palladium is very slightly attacked by boiling and concentrated hydrochloric and sulphuric acids. It dissolves in nitric acid, communicating a brownish red colour to the acid, while no gas is evolved if the temperature is low, the nitric acid being converted into nitrous acid. Palladium dissolves with facility in aqua-regia; its surface is blackened by tincture of iodine, which has no effect upon platinum.

Palladium is sometimes used for making the divided scales of astronomical instruments; being nearly as white as silver, and not blackened by sulphurous emanations, it is well adapted for that purpose. An alloy of palladium with 1-10th of its weight of silver is used by dentists.

Palladium has a much greater affinity for oxygen than platinum. It forms two oxides, the *protoxide* PdO, and the *bioxide* PdO_2.

Protoxide of palladium, Palladous oxide, PdO, 61·27 *or* 765·9.—This oxide is obtained by dissolving palladium in nitric acid, evaporating the solution to dryness, and calcining the nitrate at a gentle heat. It forms a black mass, which dissolves with difficulty in acids. When carbonate of potash or soda is added in excess to a palladous salt, the hydrated protoxide precipitates of a very dark brown colour. This oxide is easily deprived of its water by heat, but a violent calcination is necessary to reduce it to the metallic state.

The palladous salts are for the most part brown or red; their taste is astringent, but not metallic. When ignited alone, or when gently heated in hydrogen gas, they yield metallic palladium. The metal is precipitated from the solutions of palladous salts by *phosphorus*, by *sulphurous acid*, by *nitrite of potash*, by all the *metals* which reduce silver, by *formiate of potash*, and by *alcohol* at a boiling heat. *Hydrosulphuric acid* and *hydrosulphate of ammonia* throw down the brown sulphide of palladium, insoluble in the latter reagent. *Hydriodic acid* and *iodide of potassium* throw down a black precipitate of iodide of palladium, visible even to the 500,000th degree of dilution. This reaction serves for the separation of iodine from bromine; for alkaline bromides do not precipitate palladous salts. *Potash* or *soda* forms a brown precipitate of a basic salt, soluble, with the aid of heat, in excess of the reagent. *Ammonia* produces no precipitate in a solution of palladous nitrate; but from a solution of the chloride it throws down a flesh-coloured precipitate of ammonio-chloride of palladium, soluble in excess of ammonia. The *carbonates of potash* and *soda* form a brown precipitate of hydrated palladous oxide. Carbonate of ammonia acts like ammonia. *Phosphate of soda* forms a brown precipitate. *Ferrocyanide* and *ferricyanide of potassium* form no precipitates, but the liquid after a while coagulates into a jelly. *Cyanide of mercury* throws down a white precipitate of cyanide of palladium. *Protochloride of tin* forms a black precipitate, which dissolves with intense green colour in hydrochloric acid. *Protosulphate of iron* precipitates palladium slowly from the nitrate, but not from the chloride. The reactions of palladium with hydrosulphuric acid, cyanide of mercury, and iodide of potassium taken together, serve to distinguish it from all other metals.

Protosulphide of palladium, PdS, is obtained by precipitating a palladous salt by hydrosulphuric acid, and is of a dark brown colour; it may also be prepared by the direct union of its elements.

Protochloride of palladium, PdCl, is prepared by dissolving palladium in hydrochloric acid, to which a little nitric acid is added, and evaporating the solution to dryness, to expel the excess of acid. The compound is a mass of a dark brown colour, which becomes black when made anhydrous by heat, and may be fused in a glass vessel. When heated in platinum vessels, it becomes contaminated with the protochloride of that metal. When dissolved with chloride of potassium, it forms a double salt, KCl . PdCl, which is soluble in cold, and considerably more so in hot water, and crystallises in four-sided prisms, of a dull yellow colour. Protochloride of palladium also combines with chloride of ammonium and chloride of sodium, according to Bonsdorff, and forms double salts with most other chlorides.

Protocyanide of palladium, PdCy, is always formed when cyanide of mercury is added to a neutral solution of palladium, as a light-coloured precipitate, which becomes grey after drying. When the solution of palladium is acid, no precipitate is formed, and when the solution contains copper, the precipitate has a green colour. Palladium appears to have a greater affinity for cyanogen than any other metal. Even cyanide of mercury is decomposed when boiled with protoxide of palladium, and cyanide of palladium formed. When this cyanide is dissolved in ammonia, and the excess of the latter allowed to escape by evaporation, a precipitate of brilliant, colourless, crystalline plates is formed, which appears to consist of ammoniacal cyanide of palladium.

Nitrate of palladium, $PdO . NO_5$, is formed by dissolving the metal in nitric acid; the solution dries up into a dark red saline mass. When an excess of ammonia is added to an acid solution of this salt, and the solution evaporated by a gentle heat, a colourless nitrate of palladium and ammonium is deposited in rectangular tables.

Bioxide of palladium, Peroxide of palladium, Palladic oxide, PdO_2, 69·27 *or* 865·9.—To prepare this oxide, Berzelius recommends a solution of the hydrate or carbonate of potash to be added by small quantities at a time, to the dry bichloride of palladium and potassium, mixing well after each addition. A yellowish brown powder separates, which is the hydrated bioxide, retaining a little alkali. Washed with boiling water, it loses the greater part of its combined water and becomes black. This oxide dissolves with difficulty in acids; the solutions are yellow. The corresponding bisulphide of palladium has not been formed.

Bichloride of palladium, $Pd\,Cl_2$, is obtained in solution, when the protochloride is dissolved in concentrated aqua-regia, and the solution only slightly heated. Its solution is of so dark a brown as to appear black, and gives a red precipitate with chloride of potassium. When the solution is diluted or heated, chlorine gas is evolved, and protochloride of palladium reproduced. The double salt of this chloride and chloride of potassium is obtained by treating the double protochloride of palladium and potassium in fine powder with aqua-regia, and evaporating the supernatant fluid to dryness. It forms a cinnabar red powder, in which little octohedral crystals can be perceived, both the palladic and palladous double chlorides being isomorphous with the corresponding compounds of platinum. When treated with hot water, this double salt emits chlorine, and is in a great measure decomposed. The salts of bioxide of palladium are scarcely known.

Ammoniacal compounds of palladium.—A moderately concentrated solution of protochloride of palladium treated with a slight excess of ammonia, yields a beautiful flesh-coloured or rose-coloured precipitate, consisting of NH_3PdCl. This precipitate dissolves in a larger excess of ammonia; and the ammoniacal solution, when treated with acids, yields a yellow precipitate having the same composition. This yellow modification is likewise obtained by heating the red compound in the moist state to 212°, or in the dry state to 392°. The yellow compound dissolves abundantly in aqueous potash, forming a yellow solution, but without giving off ammonia, even when the liquid is heated to the boiling point; the red compound behaves in a similar manner, but, before dissolving, is converted into the yellow modification. For this reason, Hugo Müller, who has lately made the ammoniacal compounds of palladium the subject of an elaborate examination, regards the red compound as *ammonio-palladous chloride*, $NH_3 . PdCl$, and the yellow, as *chloride of palladammonium*, $\overbrace{NH_3Pd} . Cl$. The yellow compound, digested with water and oxide of silver, yields the *oxide of palladammonium* (or *palladamine*), $NH_3Pd.O$. This compound is a strong base, analogous to *oxide of platammonium* (p. 374). It is soluble in water, to which it communicates a strong alkaline taste and reaction; by evaporating the solution in vacuo, the base is obtained in the form of a crystalline mass, which absorbs carbonic acid rapidly from the air, especially when moist. It unites with acids, forming definite salts. Its solution precipitates the salts of silver and copper, and an excess of it does not redissolve the precipitates. *Sulphite of palladammonium*, $\overbrace{NH_3Pd} . SO_3$, is formed by saturating the solution of the oxide with sulphurous acid, or by the action of that acid on the yellow chlorine-compound: it crystallises in orange-yellow octohedrons. The *sulphate*, $\overbrace{NH_3Pd} . SO_4$, crystallises in a similar manner. The nitrate, iodide, and bromide have also been formed. The *fluoride* is obtained by adding the chloride to a solution of fluoride of silver.

Chloride of ammopalladammonium (or *chloride of pallad-diamine*, according to Müller),

$$2NH_3 . PdCl = NH_2\overbrace{(NH_4)\,Pd} . Cl,$$

separates from the ammoniacal solution of chloride of palladammonium, in colourless, oblique rhombic prisms, which at 392° give off half their ammonia and are reduced to $NH_3Pd . Cl$. The *iodide* and *bromide* of ammopalladammonium are likewise obtained by treating the solutions of iodide and bromide of palladium or palladammonium with ammonia. They both crystallise readily. The *fluoride* is obtained by adding ammonia to the solution of chloride of palladammonium in fluoride of silver, and evaporating: it forms oblique rhombic prisms. The *silico-fluoride* is obtained in crystalline scales on adding hydrofluosilicic acid to any soluble salt of ammopalladammonium. *Oxide of ammopalladammonium*, $\overbrace{NH_3Pd} . O$.—By decomposing the solution of the chloride with oxide of silver,—or better, the sulphate with hydrate of baryta, a strongly alkaline solution is obtained, which, on evaporation, leaves the hydrated oxide in the form of a crystalline mass, though not quite pure. The solution precipitates the salts of aluminium, iron, cobalt, nickel, and copper, but not those of silver; expels ammonia from chloride of ammonium, on boiling; and absorbs carbonic acid from the air. The *carbonate* obtained in this manner, or by decomposing the chloride with carbonate of silver, or the sulphate with carbonate of baryta, crystallises in shining, colourless prisms, which turn yellow a little above 212°; the solution is strongly alkaline, and gives copious precipitates with salts of lime, baryta, copper, and silver. The *sulphite*, $\overbrace{NH_2(NH_4)Pd} . SO_3$, obtained by direct combination, or by the action of ammonia on sulphite of palladammonium, forms small prismatic crystals, sparingly soluble in water, insoluble in alcohol, and turning yellow at about 392°. The *sulphate* obtained by treating palladous sulphate with excess of ammonia, forms small colourless prisms, easily soluble in water, but insoluble in alcohol (Hugo Müller).*

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* Ann. Ch. Pharm. lxxxvi. 341.

ESTIMATION AND SEPARATION OF PALLADIUM.

Palladium is always estimated in the metallic state. It is precipitated from its solutions in the form of cyanide by means of a solution of cyanide of mercury, the liquid not containing any excess of acid. The precipitated cyanide of palladium is then reduced to the metallic state by calcination.

Palladium may be separated from nearly all other metals either by precipitation as cyanide, or by precipitation with hydrosulphuric acid, or by the solubility of its oxide in ammonia. But to separate it from copper, with which it is associated in platinum ore, the two metals are precipitated together by hydrosulphuric acid, and the precipitate, while still moist, roasted, together with the filter, as long as sulphurous acid continues to escape. The metals are thereby converted into basic sulphates, which must be dissolved in hydrochloric acid, the solution mixed with nitric acid and chloride of potassium, and evaporated to dryness. A dark saline mass is thus obtained, consisting of chloride of potassium, chloride of copper and potassium, and chloride of palladium and potassium; and on treating this mass with alcohol of sp. gr. 0·833, the two former salts are dissolved, and the double chloride of palladium and potassium remains.

SECTION III.

IRIDIUM.

Eq. 98·68, *or* 1233·5; Ir.

The black scales which remain when native platinum is dissolved in aqua-regia, were discovered by Mr. Smithson Tennant to contain iridium and osmium.* The same alloy occurs in flat white metallic grains in native platinum. Iridium has also been observed in combination with about 20 per cent. of platinum, crystallised in octohedrons, which are whiter than platinum, and are said to have a greater density, namely 22·66.

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* Phil. Trans. 1804.

The separation of the osmium and iridium is effected by the following methods: — 1. The osmide of iridium is mixed with an equal weight of common salt, and subjected to the action of a stream of chlorine in a porcelain tube heated to redness. Double chlorides of iridium and sodium, and of osmium and sodium, are then formed; and if the chlorine is moist, a certain quantity of osmic acid, which volatilises, and may be condensed in aqueous ammonia. The mixture of the double chlorides is detached from the tube and boiled with nitric acid. Osmic acid is then evolved, and may be condensed in an alkaline solution, while the chloride of sodium and iridium remains in the solution, and, when mixed with sal-ammoniac, yields a precipitate of chloride of iridium and ammonium, which, on ignition, leaves pure metallic iridium (Wöhler).—2. A mixture of 100 grammes of osmide of iridium and 300 grammes of nitre is placed in an earthen crucible, and heated to bright redness for an hour, the resulting mixture of osmiate and iridiate of potash poured out on a cold metal plate, then introduced into a tubulated retort, and distilled with a large excess of nitric acid. A large quantity of osmic acid then volatilises and condenses in the receiver in beautiful white crystals. As soon as the evolution of osmic acid ceases, water is added, and the residue, consisting of oxide of iridium, with a certain quantity of oxide of osmium, is collected on a filter and boiled with aqua-regia, which dissolves the two metals as chlorides. The solution is then mixed with sal-ammoniac, which precipitates chloride of osmium and ammonium, and bichloride of iridium and ammonium; and the mixed precipitate suspended in water and exposed to a current of sulphurous acid, whereby the compound

$IrCl_2.NH_4Cl$, is converted into $IrCl.NH_4Cl$, which dissolves, while the chloride of osmium and ammonium remains unaltered and does not dissolve: this latter chloride yields pure metallic osmium by calcination. The solution of protochloride of iridium and ammonium leaves, when evaporated, beautiful brown crystals, which yield metallic iridium by calcination.

Iridium is obtained immediately from the chloride, by decomposing that salt with hydrogen at a gentle heat, or by exposing it alone to a very high temperature, in the form of a grey metallic powder, much resembling spongy platinum; also, as above described, from the chloride of iridium and ammonium. It is one of the most refractory bodies known, not being fused by the oxyhydrogen blowpipe. Mr. Children, however, succeeded in fusing a portion of iridium into a globule, by the discharge of a very large voltaic battery. This globule was white and very brilliant, but still a little porous; its density was 18·68. Iridium is neither ductile nor malleable; but it may be obtained in the form of a compact mass, very hard, and capable of taking a good polish, by moistening the pulverulent metal with a small quantity of water, compressing it lightly at first with filtering paper, afterwards very forcibly in a press, and calcining it at a strong white heat in a forge fire. The metal thus aggregated is very porous, and its density does not exceed 16·0. Iridium becomes white and brilliant by strong ignition, without fusion, and is afterwards insoluble in acids. If reduced by hydrogen at a low temperature, it oxidates slowly when heated to redness, or when digested in aqua-regia. This metal is generally rendered soluble by one or other of the following operations. It is calcined with hydrate of potash or nitre, or with a mixture of these salts, which gives a compound of sesquioxide of iridium and potassium. Or, the metal is reduced to a fine powder, and intimately mixed with an equal weight of chloride of potassium or sodium, and the mixture heated to low redness in a stream of chlorine gas. The metal then combines with chlorine, and the double chloride of iridium and potassium or sodium is formed, which is soluble in water.

Oxides of iridium.—Iridium forms four compounds with oxygen, which are obtained by decomposing the corresponding chlorides. The *protoxide of iridium*, IrO, is obtained from the chloride produced when iridium is heated in chlorine gas; also by precipitating the double chloride of iridium and potassium (KCl . IrCl) with carbonate of potash. The hydrate is then obtained of a greenish grey colour, which is soluble in an excess of the alkaline carbonate. This oxide is the base of a class of salts. The *sesquioxide of iridium*, Ir_2O_3, is formed when the metal is calcined with hydrate of potash or nitre. Berzelius recommends as the best process for procuring it, to mix the double bichloride of iridium and potassium ($KCl + IrCl_2$) with twice its weight of carbonate of potash, and expose it to a low red heat. On dissolving out the alkaline salt, the sesquioxide remains as a very fine powder, of a black colour with a shade of blue. A heat above the melting point of silver is required to expel the oxygen from this oxide. It is reduced to the metallic state by hydrogen gas at the usual temperature, an effect which appears to arise from the oxide of iridium having the property, as well as the metal, to determine the oxidation of hydrogen, a reaction which causes the oxide to be heated to the temperature at which it is itself reduced by hydrogen. The hydrate of this oxide dissolves in acids and forms a particular class of salts, the solutions of which are sometimes of a very dark colour, resembling a mixture of water and venous blood.

Bioxide of iridium, or Iridic oxide, IrO_2.—A solution of sesquichloride of iridium mixed with potash yields no precipitate at first; but if the liquid be heated out of contact with the air, it quickly assumes an indigo colour, absorbs oxygen from the air, and deposits hydrated iridic oxide, $IrO_2 . 2HO$, which may be rendered anhydrous by calcination. This oxide is likewise obtained by dissolving the hydrated sesquioxide in potash, and treating the solution with an acid. A greenish-blue precipitate is then formed, which gradually absorbs oxygen from the air, and assumes an indigo colour (Claus). This oxide forms salts whose solutions are of a dark, brown-red colour and almost opaque when concentrated, but reddish-yellow when dilute. *Hydrosulphuric acid* decolorises the solutions at first, and afterwards forms a brown precipitate; *hydrosulphate of ammonia* also forms a brown precipitate. *Potash* and *ammonia* decolorise the solution, and produce only a slight black precipitate; but the liquid, on exposure to the air, soon acquires a very fine blue colour. *Carbonate of potash* forms a red-brown precipitate, which gradually dissolves, the liquid afterwards turning blue when exposed to the air. *Carbonate of ammonia* imparts a blue colour to the liquid under the influence of the air. *Chloride of ammonium* forms a dark, cherry-red pulverulent precipitate of bichloride of iridium and ammonium. *Ferrocyanide of potassium* and *protosulphate of iron* decolorise the solution. *Protochloride of tin* forms a light brown precipitate. *Zinc* precipitates metallic iridium as a black powder.

Teroxide of iridium, IrO_3, is formed in small quantity when the alloy of osmium and iridium fused in nitre is digested in aqua-regia. The double terchloride of iridium and potassium then formed yields a rose-red solution, which, when treated with an alkali, slowly deposits the teroxide as a greenish-yellow precipitate, retaining, however, a certain quantity of the alkali. The salts of the protoxide and teroxide afford blue and purple solutions when mixed, depending probably on the formation of one or more combinations of these oxides. The name iridium (from Iris) was applied to this metal, from the variety of colours which its preparations exhibit.

Sulphides of iridium, corresponding with the oxides of the same metal, have been formed.

Chlorides of iridium.—The *protochloride*, IrCl, is formed when iridium in powder is heated to low redness in chlorine gas. As thus prepared, it is insoluble in water, but slightly soluble in hydrochloric acid. It forms double salts with the chlorides of potassium, ammonium, and sodium.

The *sesquichloride*, Ir_2Cl_3, is prepared by dissolving the sesquioxide in hydrochloric acid. It is black, deliquescent, and does not crystallise. It forms soluble double chlorides, which are decomposed by ebullition into iridous double chlorides (containing IrCl), which remain in solution, and iridic double chlorides (containing $IrCl_2$), which are precipitated. Claus has obtained the compounds, $3KCl . Ir_2Cl_3 + 6HO$; $3NH_4Cl . Ir_2Cl_3 + 3HO$; and $3NaCl . Ir_2Cl_3 + 24HO$.

The *bichloride*, $IrCl_2$, is obtained by dissolving very finely-divided iridium, or one of its oxides, in aqua-regia, the liquid being heated to the boiling point. It dissolves in water, forming a reddish-yellow solution. It combines with other chlorides, forming very definite salts. The potassium-salt, *chloridiate of potassium*, $IrCl_2 . KCl . HO$, crystallises in black octohedrons, yielding a red powder, and soluble in water, to which it imparts a red colour. *Chloridiate of ammonium*, $IrCl_2 . NH_4Cl . HO$, is obtained, on mixing the solutions of the two chlorides, as a very dark brown precipitate, which dissolves in boiling water, and crystallises in octohedrons on cooling. Its colouring power is very great, 1 part of it sufficing to impart a distinct coloration to 40,000 parts of water. The red colour often exhibited by chloroplatinate of ammonium is due to traces of this salt. Chloridiate of ammonium dissolves in sulphurous acid, and is thereby converted in a soluble and crystallisable compound of NH_4Cl, and IrCl; the separation of iridium and osmium depends upon this property. Bichloride of iridium, free or combined with other chlorides, is also reduced to the state of protochloride by potash, hydrosulphuric acid, ferrocyanide of potassium, and alcohol. According to Claus,* the bichloride is converted by potash into the olive-green sesquichloride, hypochlorite of potash being formed at the same time. The alkaline solution when heated becomes colourless, and afterwards violet-red, and yields a blue precipitate of the hydrated bioxide; the decolorised alkaline solution, mixed with a few drops of alcohol and heated, deposits metallic iridium. Nitrate of silver added to the solution of the bichloride forms a blue precipitate, which quickly loses its colour and passes into the compound $Ir_2Cl_3 . 3AgCl$. Mercurous nitrate forms a light ochre-yellow precipitate of $Ir_2Cl_3 . 3Hg_2Cl$.

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* Liebig and Kopp's Jährebericht, 1855, p. 427.

Terchloride of iridium, $IrCl_3$, is formed by treating an oxide or a lower chloride of iridium with very strong aqua-regia, at a temperature not exceeding 104° or 122° (40° or 50° C). Its colour is a deep brown, nearly approaching to black; it is soluble in water, and deliquescent. It forms double chlorides with the chlorides of the alkali-metals.

Carburet of iridium.—When a coherent mass of iridium is held in the flame of a spirit lamp, black masses appear on its surface, which are a carburet, containing 19·83 per cent. of carbon, or IrC_4. The carbon burns off readily in the air.

Iridic sulphate is obtained by dissolving bisulphide of iridium in nitric acid and expelling the excess of acid by evaporation. It dissolves in water and alcohol, forming orange-yellow solutions, which on evaporation leave the salt in the form of a syrupy uncrystallisable mass.

AMMONIACAL COMPOUNDS OF IRIDIUM.—*Ammonio-iridious chloride*, $NH_3 . IrCl$, or *Chloride of iridammonium*, $N\overbrace{H_3Ir} . Cl$. —Prepared by heating bichloride of iridium till it is converted into protochloride, dissolving the brown resinous residue in carbonate of ammonia, and adding hydrochloric acid in slight excess. The compound then separates in the form of a yellow granular precipitate, insoluble in water. The oxide corresponding to this chloride has not been obtained in the free state. The *sulphate* $N\overbrace{H_3Ir} . SO_4$ is obtained by heating the chloride with dilute sulphuric acid. It crystallises in large orange-yellow laminæ, easily soluble in water. *Biammonio-iridious chloride,* $2NH_3 . IrCl$, or *Chloride of ammiridammonium,* $\overbrace{NH_2(NH_4)Ir} . Cl$, is obtained, as a white precipitate, by boiling the compound, $NH_3Ir . Cl$, with excess of ammonia. Treated with moderately strong sulphuric acid, it yields the corresponding sulphate, $\overbrace{NH_2(NH_4)Ir} . SO_4$, in rhombic prisms; and, by decomposing this salt with nitrate of baryta, or decomposing the chloride with nitric acid, the nitrate is obtained in yellow needles, which dissolve readily in water, melt when heated, and then suddenly decompose with flame. A *chloronitrate of ammiridammonium,* $\overbrace{NH_2(NH_4)Ir} . \left\{ \begin{matrix} NO_6 \\ Cl \end{matrix} \right.$, or *nitrate of ammochloriridammonium,* $\overbrace{NH_2(NH_4)(IrCl)}.NO_6$, analogous to Gros's platinum-nitrate (p. 379), is obtained as a yellowish, crystalline, granular mass, by heating the chloride of iridammonium, $NH_3Ir . Cl$, with strong nitric acid; when recrystallised from water, it forms shining yellow, laminar crystals. *Bichloride of ammiridammonium,* $\overbrace{NH_2(NH_4)Ir} . Cl_2$, or *chloride of ammo-chloriridammonium,* $\overbrace{NH_2(NH_4)(IrCl)} . Cl$, is obtained by treating the last-mentioned salt with hydrochloric acid, in the form of a violet precipitate, which dissolves readily in hot water, and separates from the solution in violet crystals. Nitrate of silver added to the solution throws down only half the chlorine. The nitrate, treated with dilute sulphuric acid, yields the chlorosulphate of ammiridammonium in delicate greenish, needle-shaped crystals (Skoblikoff).

The compound $5NH_3 . IrCl_3$, or $\left. \begin{matrix} \overbrace{NH_2(NH_4)Ir} \\ \overbrace{NH(NH_4)_2Ir} \end{matrix} \right\} Cl_3$, is obtained by mixing a dilute solution of $Ir_2Cl_3 + 3NH_4Cl$, mixed with excess of ammonia, and leaving the mixture in a well-closed and completely filled bottle for some weeks in a warm place; heating the liquid, which has then acquired a rose-colour, to expel the excess of ammonia; neutralising with hydrochloric acid; evaporating to dryness; and treating the greenish yellow residue with cold water to extract the chloride of ammonium. A light flesh-coloured, finely crystalline powder then remains, which, when dissolved in boiling water, acidulated with hydrochloric acid, yields, on cooling, a crystalline precipitate of $5NH_3 . Ir_2Cl_3$ mixed with sesquichloride of iridium. This compound when dissolved in a boiling solution of ammonia, is partially decomposed, with separation of blue hydrated bioxide of iridium; when digested with water and oxide of silver, it yields a rose-coloured alkaline solution of the base $5NH_3 . Ir_2O_3$. This solution, saturated with various acids, yields:—the *carbonate*, $5NH_3 . Ir_2O_3 . 3CO_2 + 3HO$, in the form of a finely crystalline powder, having a light flesh-colour and alkaline reaction; the *nitrate*, $5NH_3 . Ir_2O_3 . 3NO_5$, in indistinct, light flesh-coloured, neutral prisms; and the *sulphate*, $5NH_3 . Ir_2O_3 . 3SO_4$, as a neutral crystalline salt of similar colour. All these salts are soluble in water (Claus).

ESTIMATION AND SEPARATION OF IRIDIUM.

The quantitative estimation of iridium is effected in the same manner as that of platinum, viz. by precipitating with sal-ammoniac and igniting the precipitate. The same method serves to separate iridium from all the preceding metals except platinum. The separation of these two metals is effected by the method already described for the preparation of pure platinum (p. 336); viz. by precipitating with chloride of potassium, fusing the precipitate with carbonate of potash, and dissolving out the platinum with aqua-regia.

SECTION IV.

OSMIUM.

Eq. 99·56 *or* 1244·5; Os.

In the treatment of the alloy of iridium and osmium, the latter is separated as a volatile oxide, or osmic acid (p. 394). To obtain the metal, a solution of osmic acid is mixed with hydrochloric acid, and digested with mercury in a well closed bottle at a temperature of 104° (40° Cent.). The osmium is reduced by the mercury, and an amalgam formed, which is distilled in a retort, through which a stream of hydrogen is passed, till all the mercury and calomel formed are removed: osmium then remains as a black powder without metallic lustre. Metallic osmium is also obtained by igniting the sesquichloride of osmium and ammonium mixed with sal-ammoniac.

When rendered coherent, osmium is a white metal, less brilliant than platinum, and very easily pulverised. Its density is about 10. As obtained from the amalgam, osmium is highly combustible; when a mass of it is ignited at a point, it continues to redden, and burns without residue, being converted into the volatile oxide or osmic acid. Osmium in the same condition is oxidated by nitric acid or aqua-regia, and the osmic acid formed distills over with the water and acid. But after being exposed to a red heat, osmium becomes much less combustible in air, and is not oxidated by the humid way, resembling silicon and titanium in that respect. Six different oxides of this metal have been obtained, namely, OsO; Os_2O_3; OsO_2; OsO_3; OsO_4; and OsO_5. The three lowest of these oxides are analogous in composition to the oxides of iridium.

Chlorides and oxides of osmium.—When osmium is heated in a long glass tube by a spirit lamp, and chlorine gas passed over it, two chlorides are formed, which condense separately in the tube, owing to a difference in their volatility. The *protochloride*, OsCl, which is the least volatile, crystallises in needles of a deep green colour. It is deliquescent, and forms a green solution remarkable for its beauty. This solution is instantly discoloured by great dilution, metallic osmium being deposited, and hydrochloric and osmic acids remaining in solution. Chloride of osmium combines with alkaline chlorides, and acquires greater stability. The *protoxide*, OsO, is obtained by adding potash to a solution of protochloride of osmium and potassium; after some hours, a deep green, almost black, powder is precipitated, which is the hydrated oxide. This hydrate contains alkali. It dissolves slowly but completely in acids, and gives solutions of a deep green colour.

Sesquioxide of osmium, Os_2O_3, is not known in the separate state; but when a mixture of osmic acid and ammonia is kept for some hours at a temperature of 100° to 120°, nitrogen gas is evolved, and a black substance is deposited, containing the sesquioxide in combination with ammonia. It dissolves slowly in acids, and forms yellowish brown solutions, which become brown-black when they contain much oxide. The metal is not precipitated from these solutions by zinc or iron. The corresponding *sesquichloride of osmium* is obtained in combination with chloride of potassium as a double salt, when the preceding oxide containing ammonia is dissolved in hydrochloric acid, and evaporated to dryness; the compound is not crystalline.

Bichloride of osmium, $OsCl_2$, is the more volatile chloride produced when osmium is heated in chlorine. It condenses as a dark red floury powder. Exposed to air, it attracts a little moisture, and forms dendritic crystals. It is soluble in a small quantity of water, giving a yellow solution, but is decomposed by a large quantity, like the protochloride. The bichloride of osmium and potassium is prepared in the same manner as the corresponding salt of iridium. In powder, it is of a red colour like minium, but forms also the usual octohedral crystals, $KCl . OsCl_2$, which are brown. A solution of this double salt, mixed with carbonate of potash or soda, affords after a time, or immediately, if heated, the corresponding *bioxide of osmium* or *osmic oxide*, OsO_2, as a brown powder, which appears black when collected. This oxide, like the peroxide of iridium, is reduced by hydrogen at ordinary temperatures. It is a base capable of uniting with acids at the moment of its formation.

Osmic sulphate is obtained by treating one of the sulphides of osmium with nitric acid; when dried as completely as possible, it forms a dark yellowish brown syrup, which dissolves in water. The reactions of osmic salts (*e. g.* of the bichloride of osmium and potassium) in solution, are as follows:—*Potash* forms a black precipitate, slowly in the cold, immediately on boiling; *ammonia*, a brown precipitate, after some time; *carbonate of potash*, the same; *chloride of ammonium*, a red precipitate; *protochloride of tin*, a brown precipitate; *mercurous nitrate*, yellowish white; *nitrate of silver*, dark olive-green; *hydrosulphuric acid*, a yellowish brown precipitate after some time; *hydrosulphate of ammonia*, a yellowish brown precipitate insoluble in excess. No precipitate is formed by oxalic acid, ferrocyanide or ferricyanide of potassium, or ferrous sulphate. *Zinc* throws down part of the osmium in the metallic state. *Iodide of potassium* does not form any precipitate, but imparts a deep purple-red colour, which does not disappear when the liquid is heated. *Tannic acid* imparts a deep blue colour.

Osmious acid, OsO_3.—This acid is not known in the separate state, being resolved at the moment of separation from its combinations, into osmic acid and osmic oxide, $2OsO_3 = OsO_4 + OsO_2$. *Osmite of potash*, $KO . OsO_3 + 2HO$, is obtained by the action of reducing agents on the osmiate; thus, when a few drops of alcohol are added to a solution of osmiate of potash, the osmite is precipitated in the form of a rose-coloured crystalline powder, a strong odour of aldehyde being at the same time evolved, due to the oxidation of the alcohol. Osmite of potash may be obtained in octohedral crystals of considerable size, by mixing a solution of osmiate with nitrite of potash, and leaving the mixture to evaporate slowly. The salt is likewise obtained by dissolving osmic oxide in osmiate of potash. It is rose-coloured, soluble in water, insoluble in alcohol and ether, permanent in dry air, but changes into osmiate under the influence of air and water. Chlorine converts it into osmic oxide and osmiate of potash. It is decomposed by acids, even by the weakest, osmic oxide being precipitated and osmic acid evolved. Sulphurous acid introduced into a solution of this salt, previously rendered alkaline, throws down a yellow crystalline precipitate, containing a salt whose acid is formed of osmium, oxygen, and sulphur. Chloride of ammonium decomposes osmite of potash, forming a nearly insoluble yellow salt, $NH_4Cl . OsO_2NH_2$, which may be regarded as a compound of sal-ammoniac with *osmiamide*, OsO_2NH_2. This compound, heated in a stream of hydrogen, gives off ammonia and sal-ammoniac, and leaves metallic osmium. *Osmite of soda* is prepared in the same manner as osmite of potash, but does not crystallise so easily; its solutions are rose-coloured. Osmious acid does not combine with ammonia; the osmites of potash and soda are rapidly reduced by ammonia.

A *terchloride of osmium* has been obtained in combination with chloride of ammonium, as a double salt, when osmic acid is saturated with ammonia, and treated after a while with excess of hydrochloric acid, mercury being also placed in contact with it. After a few days, the liquid loses the odour of osmic acid, and when evaporated to dryness, leaves the double salt in brown dendritic crystals.

Osmic acid, OsO_4, or the volatile oxide of osmium, is best obtained by the combustion of osmium in a glass tube through which a stream of oxygen gas is passed; it is also obtained by the action of nitric acid on osmium, and in the decomposition of osmites or osmates by acids. It condenses in long, colourless, regular prismatic needles. The odour of this compound is extremely acid and penetrating, resembling that of the chloride of sulphur. It was from this property of its acid, which is so constantly observed when the oxidable compounds of osmium are heated in air, that osmium obtained its name (from *ὀσμος*, odour). Its taste is acrid and burning, but not acid. It becomes soft like wax by the heat of the hand, melts into a colourless liquid like water considerably below 212°, and enters into ebullition a very little above its point of fusion. It is dissolved slowly, but in considerable quantity, by water. The solution has no acid reaction. Osmic acid is also soluble in alcohol and ether, but these solutions are apt to deposit metallic osmium. It is a weak acid, being incapable of displacing carbonic acid from the carbonates, in the humid way, but forms a class of salts, the osmiates. Osmic acid is expelled by heat from most of its combinations with bases.

An acid containing more oxygen than osmic acid, and apparently having the formula OsO_5, is formed by submitting the osmiates to the action of oxygen and oxidising agents. It is very unstable; its potash and soda-salts have a dark brown colour, and sometimes crystallise in the alkaline liquids. If the formula OsO_5 be correct, the oxidation-series of osmium will present remarkable analogies with those of nitrogen, phosphorus, and arsenic (Fremy).

Osmiamic acid, Os_2NO_5.—Formed by the action of ammonia on osmic acid, $2OsO_4 + NH_3 . Os_2NO_5 + 3HO$. Its potash-salt is obtained by adding ammonia to a hot solution of osmic acid in excess of potash; the deep orange colour of the liquid soon changes to light yellow, and osmiamate of potash separates in the form of a yellow crystalline powder. The osmiamates of the alkalies and alkaline earths and the zinc-salt are soluble in water; the lead, mercury, and silver-salts insoluble. The aqueous acid is obtained by decomposing the baryta-salt with sulphuric, or the silver-salt with hydrochloric acid. It may be kept for some days when dilute, but soon decomposes in the concentrated state. It is a powerful acid, decomposing not only the carbonates, but even chloride of potassium. Fritzsche and Struve,[*] who discovered this acid, assign to it the formula Os_2NO_4, regarding it as a compound of nitride of osmium with osmic acid; $OsN . OsO_4$. Gerhardt, on the contrary,[†] assigns to it the formula above given, viz., Os_2NO_5, which is the more probable of the two, inasmuch as, if Fritzsche and Struve's were correct, the formation of the acid must be attended with the evolution of 1 eq. oxygen; but they particularly observe that no escape of gas takes place.

Sulphides of osmium.—Osmium has a great affinity for sulphur, and burns in its vapour. Five sulphides of osmium are known, corresponding to all the oxides except the highest, viz., OsS, Os_2S_3, OsS_2, OsS_3, OsS_4. The first four of these sulphides are obtained by decomposing the corresponding chlorides with hydrosulphuric acid. The tetrasulphide is prepared by passing hydrosulphuric acid gas into a solution of osmic acid: it is a sulphur-acid, completely insoluble in water; whereas the others are sulphur bases, slightly soluble in water, and forming deep yellow solutions.

ESTIMATION AND SEPARATION OF OSMIUM.

Osmium is generally estimated in the metallic state. The best mode of separating it from the metals with which it is usually accompanied, is to volatilise it in the form of osmic acid—by distillation with aqua-regia, if the compound be perfectly soluble therein, or by roasting in a stream of oxygen—receiving the vapours of osmic acid in a strong solution of potash; and to reduce this salt, by the addition of a few drops of alcohol, to osmite of potash, which is insoluble in the alcoholic liquor. The osmite of potash is then digested in a cold solution of sal-ammoniac, whereby the compound $NH_4Cl.OsO_2NH_2$ is produced, and the osmium reduced to the metallic state by igniting this last-mentioned compound in a current of hydrogen gas (Fremy).

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[*] J. pr. Chem. xli. 97.

[†] Compt. rend. de Trans. en Chimie, 1847, 304.

Another mode of proceeding is to condense the acid vapours evolved by distilling a compound of osmium with aqua-regia in a well-cooled receiver, and precipitate the osmium from the solution by metallic mercury. A precipitate is thereby obtained consisting of calomel, a pulverulent amalgam of osmium, and metallic mercury containing a very small quantity of osmium. This mixture is heated in a glass bulb, through which a stream of hydrogen is passed, whereupon the mercury and its chloride volatilise, and metallic osmium is left in the form of a black powder. The liquid, however, still retains a small quantity of osmium, which may be isolated by saturating the liquid with ammonia, evaporating to dryness, and calcining the residue (Berzelius). The osmium may also be precipitated from the distilled liquid by hydrosulphuric acid, the solution, after complete saturation, being left for several days in a stoppered bottle, till the sulphide of osmium is completely deposited. The sulphide is then washed, dried, and weighed; but as it is apt to retain moisture, and, moreover, oxidises to a certain extent in the air, the method is not very exact. It is recommended, however, for the estimation of small quantities of osmium, the method of precipitating by mercury being better adapted for larger quantities (Berzelius).

SECTION V.

RHODIUM.

Eq. 52 *or* 651·4; R.

This metal was discovered, by Wollaston, in the ore of platinum. He found the ore from Brazil to contain 0·4 per cent; native platinum from another locality has been found with as much as 8 per cent. of rhodium.

After the precipitation of the palladium from the solution of native platinum, by cyanide of mercury, the solution, in order to obtain the rhodium, may be mixed with carbonate of soda and excess of hydrochloric acid, and evaporated to dryness. The cyanide of mercury in excess is decomposed by the hydrochloric acid, and converted into chloride of mercury. The dried mass is reduced to a very fine powder, and washed with alcohol of density 0·837, which takes up the double chlorides of sodium with platinum and iridium, the copper and the mercury, but leaves the double chloride of rhodium and sodium in the form of a fine deep red powder. The rhodium is most easily reduced by gently heating the double chloride in a stream of hydrogen gas, and afterwards washing out the chloride of sodium by water.

Rhodium, when rendered coherent, is a white metal like platinum; its density is about 10·6. It is brittle and very hard, and may be reduced to powder. When pure, it is not dissolved by any acid; but when alloyed with certain metals, such as platinum, copper, bismuth, or lead, and exposed to aqua-regia, it dissolves along with those metals. When fused with gold or silver, however, it is not dissolved with the other metal. But the most eligible mode of rendering rhodium soluble, is to mix it in fine powder with chloride of potassium or sodium, and to heat the mixture to low redness in a stream of chlorine gas. A double chloride is then formed, as with the other platinum metals in similar circumstances, which is very soluble in water. The solutions of rhodium have a beautiful red colour, the circumstance from which the metal derives its name (from *ῥόδον*, a rose). Rhodium may also be rendered soluble in the dry way, by fusing it with bisulphate of potash, when the metal is oxidated with escape of sulphurous acid gas. Rhodium is the most oxidable of the platinum metals, combining with oxygen when heated to redness in an open vessel, and very readily when in fine powder and heated to a cherry-red heat. It appears to form two oxides, the rhodous and the rhodic, of which, however, the last only has been completely isolated.

Oxides of rhodium.—The *protoxide* or *rhodous oxide*, RO, is formed when rhodium is ignited in contact with the air. One hundred parts of rhodium thus treated quickly increase to 115·3 parts, corresponding to the protoxide; then slowly, if the ignition be continued, to 118·07 parts; a black powder being formed, consisting of $3RO . R_2O_3$ (Berzelius).

Rhodic oxide, R_2O_3, is produced when the metal is ignited with hydrate of potash and a little nitre, in a silver crucible. The metal swells up, assumes a coffee-brown colour, and is converted into a compound of rhodic oxide and potash, which must be washed with water, and afterwards digested in hydrochloric acid; the hydrated oxide remains of a grey colour, with a shade of green, and insoluble in acids. The same hydrated oxide, as obtained from the double chloride of rhodium and potassium or sodium, by precipitation with an alkali and evaporation, dissolves slowly in acids, together with a certain quantity of alkali which is attached to it, assuming a yellow colour, and producing double salts. The solution in hydrochloric acid is also pale, although it contains chloride of potassium, while a solution of the double chloride, prepared in the way formerly mentioned, has a fine red colour. Hence Berzelius infers that there are two isomeric modifications of this oxide, whose compounds, when in solution, are respectively yellow and rose-coloured. Hydrated rhodic oxide contains one atom of water, $R_2O_3 . HO$. Two compounds of rhodic oxide with the protoxide of the same metal appear to exist: $R_2O_3 . 3RO$, and $R_2O_3 . 2RO$. The known compounds of rhodium are not isomorphous with compounds of platinum; but this may arise from these two metals affecting combination in different proportions, so that their compounds are not analogous in composition. Their association and resemblance in other respects afford a strong presumption of their being isomorphous bodies.

Solutions of rhodic salts yield, with *hydrosulphuric acid*, a brown precipitate of protosulphide, which is slowly deposited; with *hydrosulphate of ammonia* a brown precipitate, insoluble in excess; with *sulphurous acid* and *sulphites*, a pale yellow precipitate; with *potash*, a yellow precipitate of hydrated rhodic oxide, soluble in excess; with *ammonia*, a yellow precipitate of rhodate of ammonia, which, however, does not form immediately; with *alkaline carbonates*, a yellow precipitate after a while. *Iodide of potassium* produces a slight yellow precipitate; *protochloride of tin* imparts a dark colour to the solutions, but forms no precipitate. Acetate of *lead*, *mercurous* nitrate, and nitrate of *silver* form precipitates analogous in composition to the iridium-salts already mentioned (p. 397). *Zinc* precipitates metallic rhodium. In a solution of rhodium mixed with excess of potash, *alcohol* forms, even at ordinary temperatures, a black precipitate, probably consisting of metallic rhodium; with the other platinum-metals, this reaction takes place only when the liquid is heated. No precipitate is formed by phosphate of soda, sal-ammoniac, chloride of potassium, chromate of potash, oxalic acid, cyanide of potassium, cyanide of mercury, ferrocyanide or ferricyanide of potassium, or gallic acid. *Hydrogen gas* reduces the anhydrous salts at a moderate heat.

Sulphide of rhodium.— Rhodium may be united with sulphur by either the dry or the humid way. The sulphide of rhodium was used by Wollaston to obtain the metal in a coherent mass.

Protochloride of rhodium, RCl, is obtained by heating the protosulphate (precipitated from rhodic salts by hydrosulphuric acid) in a stream of chlorine; or by digesting one of the intermediate oxides with hydrochloric acid, whereupon the sesquichloride dissolves, and the protochloride remains in the form of a reddish grey powder insoluble in water.

Sesquichloride of rhodium, R_2Cl_3, is obtained from the double chloride of rhodium and potassium, by precipitating the latter metal with fluosilicic acid. The dry salt thus obtained is brown black, and not crystalline; it requires a pretty high temperature to decompose it, and then resolves itself at once into chlorine and rhodium. This salt deliquesces in air; its solution in water is of a beautiful red colour (Berzelius). Sesquichloride of rhodium is also obtained in the form of a rose-red powder by heating the metal to low redness in a stream of chlorine (Claus). This red powder, which was regarded by Berzelius as $R_2Cl_3 . 2RCl$, is slowly decomposed when heated in hydrogen gas, is insoluble in strong hydrochloric and aqua-regia even at the boiling heat, is coloured yellow by continued boiling with potash, and if afterwards boiled with strong hydrochloric acid, dissolves in small quantity, forming a rose-coloured solution, the greater part, however, remaining unaltered.

A *chloride of rhodium and potassium*, containing $2KCl . R_2Cl_3 + 2HO$, is obtained by the action of chlorine on a mixture of rhodium and chloride of potassium, or by evaporating a solution of the sesquichloride of rhodium and sodium with chloride of potassium. It forms brown, doubly oblique prisms, which dissolve sparingly in water. Another double salt, containing $3KCl . R_2Cl_3 + 6HO$, is obtained in dark red, sparingly soluble, efflorescent prisms, by spontaneous evaporation of a solution of the hydrated sesquioxide in hydrochloric acid mixed with chloride of potassium. The *sodium double-salt*,

$3NaCl . R_2Cl_3 + 24HO$, forms doubly oblique prisms of a deep cherry-red colour. With *chloride of ammonium*, two double salts are obtained, viz., $2NH_4Cl . R_2Cl_3 + 2HO$, and $3NH_4Cl . R_2Cl_3 + 3HO$, both of which form red prismatic crystals. By precipitating either of the above double chlorides containing 2 or 3 eq. of the basic chloride to 1 eq. R_2Cl_3, with acetate of *lead*, *mercurous* nitrate, or nitrate of *silver*, rose-coloured precipitates are formed, containing 2 or 3 eq. of $PbCl$, Hg_2Cl, or $AgCl$, to 1 eq. of R_2Cl_3 (Claus).

A *sulphate of rhodium* is formed when rhodium is ignited with bisulphate of potash; it gives a yellow solution. Another sulphate in combination with sulphate of potash gradually falls as a white powder, when sulphuric acid is added to a solution of the double chloride of these bases. It is nearly insoluble in water; its formula is $KO . SO_3 + {}_2O_3 . 3SO_3$. *Nitrate of rhodium* is formed by dissolving the oxide in nitric acid. It forms a deliquescent salt of a dark red colour, $R_2O_3 . 3NO_5$; the last salt combines with nitrate of soda, forming dark red crystals soluble in water but not in alcohol: $NaO . NO_5 + R_2O_3 . 3NO_5$.

The salts of rhodium are often mixed with peculiar rose-coloured salts, whose nature is not exactly known. These new salts are not precipitated, either by iodide of potassium in the cold, or by sulphurous acid, or by ammonia; they form, with chloride of ammonium, double salts, which crystallise, not in scales, but in red prisms (Fremy).

ESTIMATION AND SEPARATION OF RHODIUM.

Rhodium is estimated in the metallic state. The solution containing it is mixed with excess of carbonate of soda and evaporated to dryness, the residue ignited, and the calcined mass treated with cold water: oxide of rhodium then remains, and may be reduced by hydrogen.

Rhodium is separated from many metals with which it may be alloyed, by fusing the alloy with bisulphate of potash; the rhodium is thereby converted into sulphate of rhodium and potassium, which may be dissolved out by water. The method of separating it from platinum and the allied metals has already been given.

The separation of rhodium from other metals in solution is somewhat difficult, because it is not completely precipitated by hydrosulphuric acid. To separate rhodium from *copper*, the solution is saturated with hydrosulphuric acid and left to stand in a stoppered bottle for twelve hours, then filtered, and the filtrate heated to separate an additional portion of sulphide of rhodium. The whole of the precipitate is then roasted in a platinum crucible till the sulphides are completely oxidised, and the product treated with strong hydrochloric acid, which dissolves the copper and leaves the oxide of rhodium. The liquid filtered from the hydrosulphuric acid precipitate still contains a small portion of rhodium, which may be precipitated by carbonate of soda and converted into oxide as above. The whole of the oxide is then reduced by hydrogen.

To separate rhodium from *iron*, the rhodium is precipitated as completely as possible by hydrosulphuric acid; the liquid filtered; and the iron in the filtrate precipitated by ammonia, after having been brought to the state of sesquioxide. The iron-precipitate carries down with it a certain portion of rhodium, which may be separated by igniting the precipitate in a current of hydrogen, and treating the reduced metals with hydrochloric acid, which dissolves the iron and leaves the rhodium: the latter is then converted into oxide by ignition in the air. The precipitated sulphide of rhodium is likewise oxidised by roasting. The small quantity of rhodium which remains in solution after precipitation by ammonia is precipitated by carbonate of soda, and converted into oxide by ignition. The whole of the oxide of rhodium is then reduced to the metallic state by hydrogen.

The separation of rhodium from the alkali-metals is easily effected by converting the metals into chlorides, and igniting the chlorides in a current of hydrogen, which reduces only the chloride of rhodium.

SECTION VI.

RUTHENIUM.

Eq. 52·1 *or* 651·25 ; Ru.

This metal was discovered by Claus in 1846. It occurs in platinum ores, chiefly in the native osmide of iridium, which contains from 3 to 6 per cent. of it. To separate it, the osmide of iridium is pulverised, mixed with about half its weight of common salt, and heated to low redness in a current of moist chlorine gas. The disintegrated mass is then digested in cold water, and the concentrated solution, which is brown-red and almost opaque, mixed with a few drops of ammonia and gently heated, whereupon it deposits a copious black-brown precipitate, consisting of sesquioxide of ruthenium and bioxide of osmium. This precipitate, after being washed with nitric acid, is heated in a retort, till the osmium is expelled in the form of osmic acid. The residue is then ignited for an hour in a silver crucible with caustic potash free from silica, and the ignited mass softened and dissolved by cold distilled water. The solution is left in a corked bottle for two hours to clarify; after which the perfectly transparent orange-coloured liquid is separated by a siphon, and neutralised with nitric acid. It then deposits velvet-black sesquioxide of ruthenium, which, when washed, dried, and ignited in an atmosphere of hydrogen, yields the pure metal.

Ruthenium is a grey metal, very much like iridium. Its specific gravity is 8·6.* It is very brittle, does not fuse even in the flame of the oxy-hydrogen blowpipe, and is scarcely attacked by aqua-regia. It combines with oxygen in four proportions, forming the three oxides, RuO, Ru_2O_3, RuO_2, and ruthenic acid, RuO_3. Its affinity for oxygen is greater than that of any of the other platinum metals, except osmium. When heated to redness in the air, it oxidises readily, forming a bluish black oxide, which does not part with its oxygen at a white heat. When fused with nitre or with caustic potash, it is converted into rutheniate of potash. It is not dissolved by fused bisulphate of potash.

Protoxide of ruthenium, RuO.—Obtained by igniting the protochloride with carbonate of soda, in a stream of carbonic acid gas, and washing the residue with water. It is a blackish grey powder, containing 13·4 per cent. of oxygen. It is insoluble in acids, and consequently its salts have not been directly formed.

The *protochloride*, RuCl, is obtained in the anhydrous state, by heating the metal to low redness in a stream of chlorine. It is a black crystalline substance, insoluble in water and acids, and imperfectly decomposed by alkalies. A soluble protochloride appears, however, to be formed by passing hydrosulphuric acid gas through a solution of the sesquichloride.

Sesquioxide of ruthenium, Ru_2O_3.—Pulverulent ruthenium, strongly heated before a powerful blowpipe turns black, and rapidly absorbs oxygen, 100 parts of the metal increasing to 118 parts; afterwards the oxidation slowly proceeds further till the oxide acquires a blackish blue colour, and contains 23 or 24 parts of oxygen to 100 parts of metal, which is about the proportion required for the sesquioxide. The *hydrated*

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* This is much less than the density usually attributed to iridium (p. 395.). It is probable, however, that the two metals do not really differ much in density; for a specimen of porous iridium prepared from the blue oxide, by reduction with hydrogen, exhibited a density of only 9·8 (Claus).

sesquioxide is formed by precipitating a solution of the sesquichloride with an alkali, by decomposing a solution of rutheniate of potash with nitric acid, or by heating the aqueous solution of the sesquichloride. It is a black-brown powder, which becomes suddenly incandescent when heated. Hydrogen gas reduces it imperfectly at ordinary temperatures. It is insoluble in alkalies, but dissolves in acids, forming orange-yellow solutions. The solution in hydrochloric acid exhibits the following reactions:—*Hydrosulphuric acid* partly precipitates the ruthenium in the form of a black sulphide, but at the same time reduces the sesquichloride to protochloride, the reduction being attended with a change of colour from orange-yellow to a fine azure blue: this reaction is extremely delicate, and very characteristic of ruthenium. *Zinc* effects the same reduction. *Hydrosulphate of ammonia* throws down the greater part of the ruthenium in the form of a black-brown sulphide, not perceptibly soluble in excess. The *caustic alkalies*, *alkaline carbonates*, and *phosphate of soda* precipitate the black sesquioxide, insoluble in excess of the reagent. *Borax* forms no precipitate at first, but, on heating the solution, the hydrated sesquioxide is thrown down. *Sulphurous acid*, *oxalic acid*, and *formiate of soda* do not precipitate the metal, but merely decolorise the solution. *Ferrocyanide of potassium* decolorises the solution at first, but afterwards turns it bluish green. Acetate of *lead* forms a purple-red precipitate, inclining to black. *Cyanide of mercury* colours the solution blue, and throws down a blue precipitate. Nitrate of *silver* forms a black precipitate, which is a mixture of chloride of silver and sesquioxide of ruthenium; the oxide dissolves, after a while, in the nitric acid, leaving a white residue of chloride of silver; and, if ammonia be then added in excess, the chloride of silver dissolves, and the sesquioxide of ruthenium is reprecipitated: this is also a very delicate reaction. The *chlorides of potassium* and *ammonium* throw down from concentrated solutions, crystalline precipitates of double chlorides, exhibiting a play of colours inclining to violet.

Sesquichloride of ruthenium, Ru_2Cl_3, is obtained in the solid state by evaporating the solution of the sesquioxide in hydrochloric acid. The residue is deliquescent, has a very astringent but not metallic taste, and dissolves in water and alcohol, forming beautiful orange-coloured solutions, but leaving a yellow basic compound undissolved. When heated, it turns green and blue. The dilute solution is resolved by heat into hydrochloric acid and the hydrated sesquioxide (pp. 414, 415). The sesquichloride forms double salts with the chlorides of potassium and ammonium, and apparently also with those of sodium and barium.

Bioxide of ruthenium, Ruthenic oxide, RuO_2, is formed by roasting and igniting the bisulphide, or by strongly igniting the sulphate, $RuO_2 . 2SO_3$; the former method yields a black-blue powder, with a tinge of green; the latter, grey particles with metallic lustre and bluish or greenish iridescence. The *hydrate*, $RuO_2 . 2HO$, is obtained as a gelatinous precipitate by decomposing the bichloride of ruthenium and potassium with carbonate of soda. The precipitate, when dried and heated in a platinum spoon, deflagrates with vivid incandescence, and is scattered about. It dissolves in acids, forming solutions which are yellow when dilute and rose-coloured when concentrated.

The *bichloride* is not known in the separate state, but forms with chloride of potassium a double salt, $KCl,RuCl_2$, which is obtained by treating the sesquichloride of ruthenium and potassium with aqua-regia. This double salt is very soluble in water, but insoluble in alcohol; its colour is brown inclining to rose-red. The aqueous solution has a deep rose-colour, strongly resembling that of sesquichloride of rhodium. Hydrosulphuric acid acts but slowly on this solution, producing first a milky turbidity from precipitated sulphur, and afterwards throwing down a yellowish brown sulphide; the solution, however, still retains a deep rose-colour and does not turn blue.

Ruthenic sulphate, $RuO_2 . 2SO_3$.—When the sulphide obtained by treating the sesquichloride with hydrosulphuric acid is digested in moderately strong nitric acid, an orange-yellow solution is formed, which, on evaporation, yields this salt in the form of a yellowish brown amorphous mass. It is deliquescent, and dissolves readily in water. Alkalies added to the solution form no precipitate at first; but, on evaporating, a yellowish brown gelatinous precipitate is obtained, consisting of hydrated ruthenic oxide, and strongly resembling impure rhodic oxide. The solution of this salt does not turn blue when treated with hydrosulphuric acid.

Ruthenic acid, RuO_3, is known only in the form of a potash-salt, which is obtained by igniting ruthenium with a mixture of potash and nitrate or chlorate of potash. It dissolves in water, forming an orange-yellow solution, which has an astringent taste, colours organic substances black by coating them with oxide, and is decomposed by acids, yielding a precipitate of the sesquioxide.

Sulphides of ruthenium.—This metal probably forms with sulphur a series of compounds analogous to the oxides; but it is difficult to obtain them in a definite state. Sulphur and ruthenium do not combine directly, and the precipitates thrown down by hydrosulphuric acid from the chlorides always contain excess of sulphur. When the sulphide obtained by precipitation from the sesquichloride is heated in an atmosphere of carbonic acid, incandescence and explosion take place, sulphur and water pass off, and a blackish grey metallic powder is left, whose analysis agrees with the formula Ru_2S_3. All the sulphides are dissolved by nitric acid of ordinary strength (Claus).

ESTIMATION AND SEPARATION OF RUTHENIUM.

This metal is precipitated from its solutions in the form of oxide, and generally as sesquioxide, viz. from a solution of the sesquichloride, either by alkalies or by simply heating the solution, and from a solution of rutheniate of potash by nitric acid. The precipitated oxide is reduced to the metallic state by ignition in an atmosphere of hydrogen. As, however, the precipitate generally contains alkali, which cannot be removed by washing, the reduced mass must be treated with water; the liquid filtered from the ruthenium; and the metal, before weighing, must be again ignited and left to cool in an atmosphere of hydrogen, as it oxidises when heated in the air. Ruthenium has hitherto been found only associated with the metals of the platinum-residues, and from these it is separated by the method described at page 413., depending on the resolution of the aqueous sesquichloride by heat into hydrochloric acid and sesquioxide of ruthenium.

NEW METHOD OF TREATING PLATINUM-RESIDUES.*

When platinum-ore has been exhausted by aqua-regia, a residue is left, commonly known by the name of *osmide of iridium.* This residue is a mixture of two different substances, one of which is scaly, and consists of osmium, iridium, and ruthenium; while the other, which is granular, contains but mere traces of osmium and ruthenium, but is very rich in iridium and rhodium. Now oxide of ruthenium can bear a red heat without decomposing, and osmium is actually roasted by the action of oxygen, producing a volatile acid, just as sulphur and arsenic do; hence the residue of platinum-ore may be decomposed by roasting; and by submitting it to this operation, osmic acid is produced in large quantity and very pure, and oxide of ruthenium is obtained in well-defined crystals. The roasting is performed as follows:—

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* Fremy, Compt. rend. xxxviii. 1008; also Traité de Chimie Générale, par Pelouze et Fremy, iii. 452.

About 200 grammes of platinum-residue (the scaly and granular alloys together) are heated to bright redness in a porcelain tube placed in a long furnace. Air is drawn through the tube by means of an aspirator, being first made to pass through solution of potash to free it from carbonic acid, and through strong sulphuric acid to remove organic matter. The air thus purified passes over the heated platinum-residue, and forms osmic acid and oxide of ruthenium. The latter crystallises in the colder parts of the roasting tube, while the more volatile osmic acid is carried forward, first into a series of empty tubes, in which part of it settles in the form of crystals, and then through two bottles filled with solution of potash, which retains the uncondensed vapours: the apparatus terminates with an aspirator. The products of the operation are:—1. Oxide of ruthenium, in violet crystals, the form of which is similar to that of native oxide of iron; 2. Osmic acid, very pure, and sometimes amounting to 40 per cent. of the platinum-residue used; 3. Osmiate of potash, which, by the addition of a few drops of alcohol, may be converted into osmite of potash, a salt from which metallic osmium may be obtained (p. 403); 4. An alloy of iridium and rhodium, which remains in the roasting tube.

This last residue may be used for the preparation of iridium and rhodium. For this purpose, it is calcined in an earthen crucible with four times its weight of nitre, care being taken not to carry the process too far; and the residue is exhausted with boiling water and filtered. A copious precipitate is thereby formed, which remains on the filter, and the filtrate consists of an alkaline liquid, which, when left to evaporate, deposits crystals of osmite of potash, the osmium never being completely removed by the previous roasting.

The precipitate which remains on the filter and retains a